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TECHNICAL PHASE REPORT

on

HIGH-TEMPERATURE PROPERTIES AND
ALLOYING BEHAVIOR OF THE
REFRACTORY PLATINUM-GROUP METALS

to

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH

August 14, 1959

by

R. W. Douglass, F. C. Holden, and R. I. Jaffee

FC

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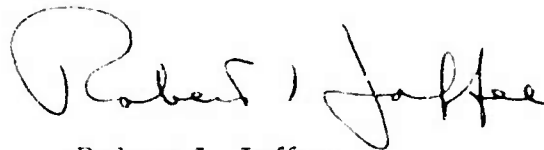
August 28, 1959

Mr. J. J. Harwood
Head, Metallurgy Branch
Department of the Navy
Office of Naval Research
Washington 25, D.C.

Dear Mr. Harwood:

Enclosed are ten copies of our Technical Phase Report, "High-Temperature Properties and Alloying Behavior of the Refractory Platinum-Group Metals", by R. W. Douglass, F. C. Holden, and R. I. Jaffee. This report covers the available literature pertinent to our effort under Contract No. NOnr-2547(00), NR 039-067. Copies also have been sent to those on the enclosed distribution list.

Yours very truly,

Robert I. Jaffee

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HIGH-TEMPERATURE PROPERTIES AND ALLOYING BEHAVIOR
OF THE REFRACTORY PLATINUM-GROUP METALS

by

R. W. Douglass, F. C. Holden, and R. I. Jaffee

INTRODUCTION

This report covers the results of a survey of the literature on the platinum-group metals. The major emphasis here is on the metallurgical properties of the four more refractory platinum-group metals, rhodium, iridium, osmium, and ruthenium; however, available information on platinum and palladium is also included. This survey is intended to provide a reference point for an investigation of the metallurgical properties of the platinum metals. It will serve as a guide to planning experimental work, both revealing areas where concentrated study is needed and preventing duplication of previous work. In general, original sources were consulted and are referred to throughout the report; however, in reviewing areas that are not of primary metallurgical interest, i.e., occurrence, extraction, and corrosion behavior, information was drawn mainly from review articles in these fields. All references are included in a list of references at the end of the report.

A selected bibliography of papers and books that proved to be of special help in compiling information for this report is included following the text. These selections are useful either in giving a broad background of the field or in supplying an extensive treatment of a specialized portion of the field.

PROCESS METALLURGY

Geologic Occurrence

The platinum metals, platinum, palladium, rhodium, iridium, osmium, and ruthenium, generally are found together in nature. The usual habitat of the metals is in ultrabasic rocks where they have been concentrated by magmatic processes. There are two principal types of primary deposits: (1) local concentrations of the native metals with dunite, often associated with chromite, and (2) disseminated in nickel-copper sulfide deposits in norite. In addition, erosion of the deposits of native platinum metals has yielded important placer deposits found in Alaska, Colombia, and the Soviet Union. Osmiridium, a natural alloy containing osmium and less than 40 per cent iridium, and iridosmine, containing greater than 40 per cent iridium, are important sources of these metals usually found in South Africa but also in Tasmania and the Soviet Union.[1,2,3]

The most important commercial dunite deposits are found in the Ural Mountains of the Soviet Union, and at Overwacht in the Transvaal in the Union of South Africa. The most extensive nickel-copper sulfide deposits yielding the platinum metals are in the norite belt of the Bushveld igneous complex in the Transvaal and in the Sudbury district of Ontario, Canada. The metals often are found in compounds in the sulfite deposits; cooperite, $Pt(As,S)_2$; sperrylite, $PtAs_2$, $PdSb_3$; laurite, RuS_2; and braggite $(Pt,Pd,Ni)S$; however, in oxide regions of the sulfide deposits, the native metals are often found.[3]

In all deposits platinum usually is found in the greatest amount, followed by palladium. The Sudbury ores usually yield platinum and palladium in equal amounts, and the natural osmium-iridium alloys yield some platinum and essentially no palladium.

To show the quantities and various sources of the metals, the production of the platinum-group metals over a span of years is listed in Table 1.[4]

The refractory platinum metals (ruthenium, rhodium, iridium, and osmium) comprise about 10 per cent of the total platinum metals production.[3] Of these, ruthenium is the most plentiful, with rhodium next most plentiful, in the ratio: ruthenium 16, rhodium 8, iridium 1, and osmium practically negligible.[10]

Extraction and Beneficiation

The refining of the platinum metals can be considered in two steps: (1) concentration of platinum metals from the ore, and (2) separation of the individual platinum metals. For native platinum and iridosmine only the second step need be used.

The most significant world source of the platinum metals is the nickel and copper sulfate ores in the Sudbury district in Canada. These ores are smelted and the metal is heated with coke and sodium bisulfate to dissolve the copper sulfide in preference to nickel sulfide. On pouring the melt, two layers are formed, the top layer containing sodium-copper sulfide and very little precious metal, and the bottom layer containing nickel sulfide and the bulk of the platinum metal. The "bottoms" are roasted and the nickel is removed by leaching with sulfuric acid, leaving a residue containing about 5 per cent platinum metals. The residue is smelted with litharge, fluxes, and charcoal, which reduce the lead oxide to molten lead. The lead, which acts as a collector for the precious metals, can be oxidized to litharge, yielding an ingot with a high concentration of the platinum metals. This is treated with boiling concentrated sulfuric acid, which removes most of the silver and about one-third of the palladium as sulfates, yielding a residue of the platinum metals and gold.[1]

This concentrate and native platinum can be dissolved in aqua regia and treated according to the flowsheet, Figure 1, to yield the platinum metals in the form of sponge and powder.

TABLE 1. WORLD PRODUCTION OF PLATINUM-GROUP METALS, 1948-1952(AVERAGE) AND 1953-1957, IN TROY OUNCES[4][a]

(Compiled by Augusta W. Jann and Bernice B. Mitchell)

Country	1948-1952 (Average)	1953	1954	1955	1956	1957
North America:						
Canada						
Platinum: Placer platinum from refining nickel-copper matte	135,112	137,545	154,356	170,494	151,357	196,077
Other platinum-group metals: From refining nickel-copper matte	160,326	166,018	189,350	214,252	163,451	213,285
United States:						
Placer platinum and from domestic gold and copper refining	30,655	26,072	24,235	23,170	21,398	18,531
Total	326,093	329,635	367,941	407,916	336,206	427,893
South America:						
Colombia: Placer platinum	30,598	29,201	28,465	27,526	26,215	26,000
Europe: U.S.S.R.:						
Placer platinum and from refining nickel-copper ores[b]	105,000	100,000	100,000	125,000	125,000	125,000
Asia: Japan						
Palladium from refineries	234	71	248	221	218	200
Platinum from refineries	--	987	1,347	628	483	425
Total	234	1,058	1,595	849	701	625
Africa:						
Belgian Congo:						
Palladium from refineries[c]	63	--	176	--	160	325
Ethiopia:						
Placer platinum	332	566	230	350[b]	300[b]	300[b]
Sierra Leone:						
Placer platinum	29	--	--	--	--	5[d]
Union of South Africa:						
Platinum-group metals from platinum ores	47,858	90,292	101,921	109,267	--	--
Concentrates (platinum-group metal content from platinum ores)	96,929	208,885	236,241	272,465	484,574	603,704
Osmiridium from gold ores	6,409	6,966	6,266	7,021	6,696	5,361
Total	151,620	306,709	344,834	389,103	491,730	609,695

TABLE 1. (Continued)

Country	1948-1952 (Average)	1953	1954	1955	1956	1957
Oceania.						
Australia:						
Placer platinum	5	- -	23	7	12	20
Placer osmiridium	53	59	16	21	26	66
New Guinea	3(e)	6	5	10	9	11
New Zealand:						
Placer platinum	2	2	1	- -	- -	- -
Papua:						
Placer platinum	1	- -	4(f)	(g)	- -	- -
Total	64	67	49	38	47	100
World Total (estimate)	615,000	775,000	850,000	950,000	980,000	1,190,000

(a) This table incorporates a number of revisions of data published in previous platinum chapters of Reference (4). Data do not add to totals shown because of rounding where estimated figures are included in the detail.

(b) Estimate.

(c) Includes platinum.

(d) Exports.

(e) Average for 4 years, only, as 1949 was the first year of commercial production.

(f) Year ended June 30 of year stated.

(g) Less than 0.5 ounce.

MINES, SUDBURY CANADA

| Electrolytic nickel refinery | Electrolytic copper refinery | Mond carbonyl nickel refinery |

PLATINUM METALS CONCENTRATES

Aqua regia

ACTON REFINERY

Flow Sheet

FILTRATE Au Pt Pd

Ferrous sulphate

BROWN GOLD

Melting

GOLD ANODES

Electrolytic refining

GOLD SPONGE

Melting
Granulation

GOLD GRAIN

FILTRATE Pt Pd

Ammonium chloride

IMPURE $(NH_4)_2 Pt Cl_6$

Ignition

IMPURE Pt SPONGE

Aqua regia
Ammonium chloride

PURE $(NH_4)_2 [Pt Cl_6]$

Ignition

PLATINUM SPONGE

FILTRATE Pd

Ammonia
Hydrochloric acid

IMPURE $[Pt (NH_3)_2 Cl_2]$

Ammonia
Hydrochloric acid

PURE $[Pd (NH_3)_2 Cl_2]$

Ignition

PALLADIUM SPONGE

FILTRATE
Traces of precious metals

Zinc reduction

PRECIOUS METALS REDUCTION RESIDUE

FILTRATE
Waste discharge

WASTE LIQUORS

RESIDUE Rh Ru Ir Ag

Smelt with silver lead, cupellation

LEAD GRAIN

Nitric acid

INSOLUBLE Rh Ru Ir

Sodium bisulphate fusion

RHODIUM SULPHATE

Sodium hydroxide

RHODIUM HYDROXIDE

Hydrochloric acid

RHODIUM CHLORIDE

Sodium nitrate
Potassium chloride

$K_3 [Rh (NO_2)_6]$

Hydrochloric acid

$K_3 [Rh Cl_6]$

Purification and reduction

RHODIUM MEAL

INSOLUBLE Ru Ir

Potassium nitrate
Potassium hydroxide (fusion)

FILTRATE Ru

Chlorine

RUTHENIUM TETROXIDE

Hydrochloric acid

RUTHENIUM CHLORIDE

Purification and reduction

RUTHENIUM MEAL

INSOLUBLE Ir

Sodium peroxide
caustic soda (fusion)

OXIDIZED IRIDIUM

aqua regia
Ammonium chloride

$(NH_4)_2 [Ir Cl_6]$

Purification and reduction

IRIDIUM MEAL

FILTRATE Pb Ag

Sulphuric acid

LEAD SULPHATE

FILTRATE Ag

Hydrochloric acid

SILVER CHLORIDE

Soda ash, charcoal smelt

SILVER ANODES

Electrolytic refining

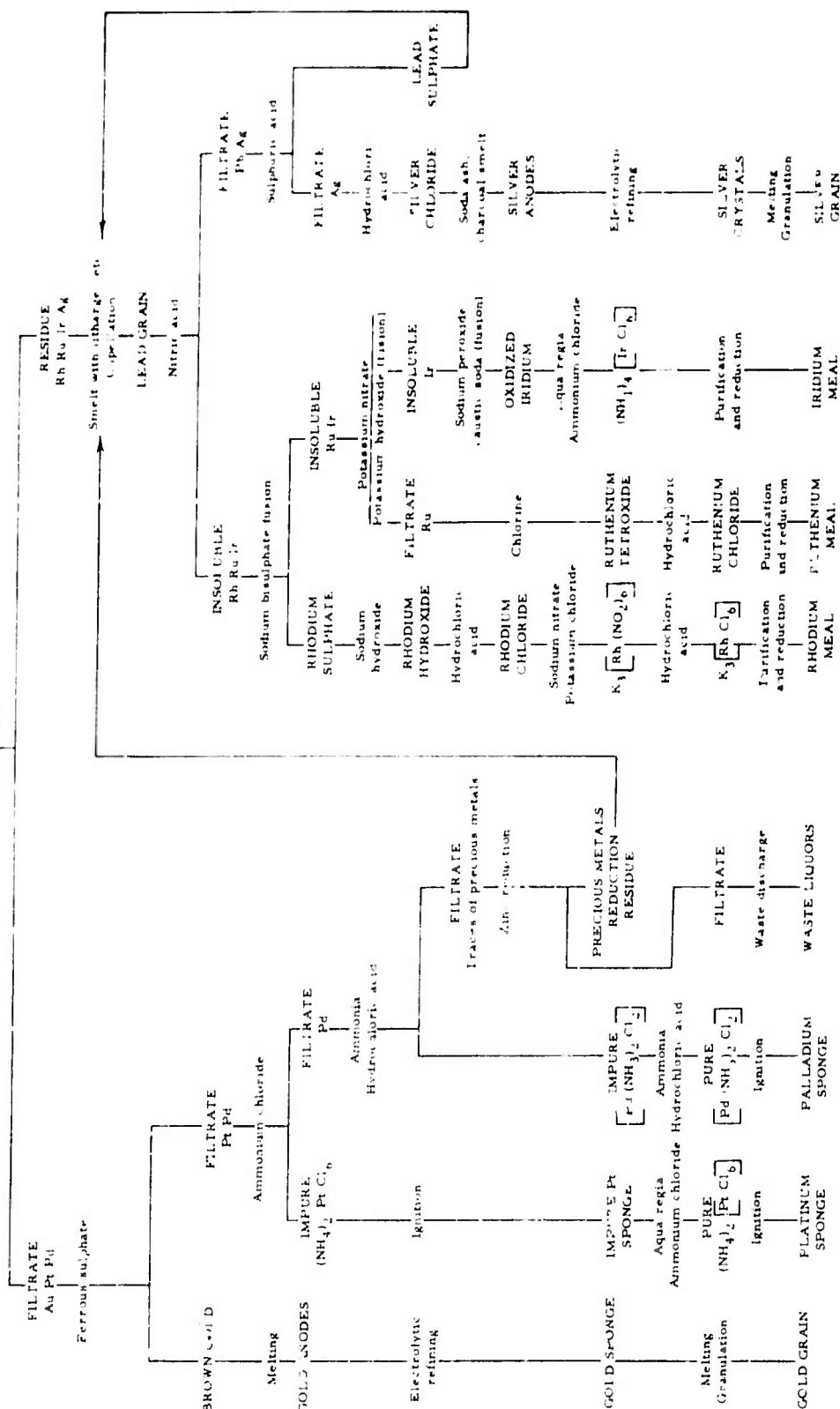SILVER CRYSTALS

Melting
Granulation

SILVER GRAIN

A 34980

FIGURE 1. FLOW SHEET FOR THE RECOVERY AND SEPARATION OF THE PLATINUM-GROUP METALS

Consolidation and Fabrication

The platinum metals, until recently, were melted in a lime crucible by direct heating with an oxyhydrogen or oxygas torch. This method, being the oldest, is perhaps most widely used, however, the use of induction heating has come into frequent use.[1,5] Arc melting under a vacuum or inert atmosphere would seem to be an efficient method of consolidation, especially for ruthenium and osmium which react readily with oxygen, however, this technique has not found commercial use.

Platinum is melted in a neutral or oxidizing atmosphere in a nonreactive crucible. Lime crucibles had been used extensively because of their availability and ability to withstand high temperatures. Zirconia crucibles are currently used in many applications, although almost any of the common high-melting refractories, such as alumina or thoria, would be acceptable. Ingot molds usually are made from graphite or silica, graphite being preferable to silica because of its good chilling properties. There are no reports in the literature on the amount of superheat necessary to provide suitable castings.

The same precautions should be taken in choosing and using a crucible or ingot mold as are taken in using platinum thermocouples or with platinum furnace windings. One important consideration is to avoid the use of a silica or silica-containing material in contact with platinum in a reducing atmosphere. In addition, a combination of oil or grease with silica in a reducing carbonaceous atmosphere will result in some reduction of silica to silicon. This then alloys with platinum to form a low-melting grain-boundary constituent.[6]

Platinum is very ductile and the ingots can be easily cold worked directly into a variety of commercial shapes. Platinum usually is forged initially at about 800 C to break down the as-cast grain structure and to provide ductility. It is customary to anneal platinum above the recrystallization temperature during cold working; however, platinum does not work harden very rapidly so that rather large reductions of the order of 75 per cent between anneals are possible.[7] Recent developments have shown that platinum prepared by powder-metallurgy techniques has superior strength to conventionally prepared platinum.[8] This will be discussed more fully later.

The melting of palladium is somewhat more difficult than that of platinum. Experience has shown that palladium melted under oxidizing conditions is gassy whereas melting in a reducing environment results in ingots that are hot short and brittle.

Atkinson[9] has studied the effect of gases on the melting, casting, and working of palladium. He reported that the use of hydrogen as a deoxidizer during melting resulted in very dense ingots, although it promotes violent gassing and attendant spattering. In addition, hydrogen dissolved in molten palladium reduces the crucible material with resultant contamination of the melt. Two other disadvantages associated with a hydrogen atmosphere are steam formation, which causes surface pitting of castings, and blister formation upon heating strip in air. Tests using city gas, methane, and acetylene as deoxidizers also showed blistering of the palladium sheet on annealing in air. The use of carbon monoxide as a deoxidizer seemed to give the best results.

An investigation of the most suitable atmosphere for annealing palladium revealed that helium and argon are the most satisfactory, followed by CO_2, steam, and

nitrogen. Hydrogen, in addition to hardening palladium, also forms blisters when the palladium is saturated with oxygen. Air is unsuitable because the oxygen reacts with hydrogen to produce blisters; where solid deoxidizers are employed, internal oxidation becomes a problem.

It appears that the use of solid deoxidizers, aluminum and calcium boride, may be superior to gaseous deoxidizers[9a], but there is no substantial information in the literature to confirm this suggestion.

Palladium, being soft and ductile, can be worked in the same manner as platinum. It is recommended that palladium be annealed in an inert atmosphere, such as nitrogen or carbon monoxide, to prevent oxide formation.[8]

Rhodium is most commonly melted by induction heating under an inert atmosphere to prevent oxide formation.[1,3] Unlike platinum and palladium, rhodium is rather difficult to work, requiring that initial reductions be accomplished at hot-working temperatures, 800 C or above.[8] Relatively ductile rhodium can be produced by hot and warm working at gradually decreasing temperatures. Sheet produced by this technique usually can be cold worked if the thickness is less than 0.030 inch; however, cold working must be accompanied by frequent annealing, as rhodium work hardens extremely rapidly at room temperature.[8]

Recent developments in electron-beam purification techniques have resulted in rhodium rods of sufficient purity to permit cold working without preliminary hot working. This work has not yet been reported in the literature and the little information that is available does not elaborate on the process.

Rhodium can be annealed in air although a superficial oxide film is formed at temperatures below 1100 C.

Iridium is generally prepared by arc-melting or powder-metallurgy techniques, although it may be melted in lime crucibles under an oxyhydrogen flame.[3]

Fabrication data for iridium prepared by powder-metallurgy techniques are not available.

Iridium is perhaps more difficult to work than rhodium. Ingot breakdown is usually accomplished at 1200 to 1500 C. Like rhodium, relatively ductile iridium can be prepared by working at gradually decreasing temperatures. Iridium can be successfully cold worked in sizes below 0.030 inch.[8]

Ruthenium and osmium, the two hexagonal members of the group, are similar with respect to their consolidation and fabrication characteristics. Both are usually consolidated by powder-metallurgy techniques, although arc melting also is employed in consolidating these metals. Neither of the metals is considered truly workable, but ruthenium has been forged in air above 1500 C, and rather small cold reductions, of the order of 10 per cent, can be effected in the laboratory.

Some success has been found in fabricating fine-grained powder-metallurgy ruthenium; however, ductile ruthenium has not yet been produced. Further research on electron-beam or floating-zone melting may produce extremely high-purity, fine-grain material, that can be successfully worked to a usefully ductile material.[10]

Rhys[10a] has reported the results of some recent work on the fabrication of ruthenium. Ruthenium powder of varying purity was investigated under a variety of sintering and working temperatures and atmospheres. Material sintered in a high vacuum had better workability than that sintered in low vacuum or a hydrogen atmosphere. Sintering temperature appeared to have little effect on workability as long as the temperature was higher than 1400 C. The hot-working temperature also did not appear to be critical, temperatures as low as 1200 C being satisfactory; however, 1450 to 1500 C forging temperatures gave optimum results. Workability was independent of furnace atmosphere, air, hydrogen, and nitrogen-hydrogen, but ruthenium encapsulated in evacuated platinum envelopes had better hot workability than unprotected ruthenium.

In general, it was possible to cold reduce ruthenium that had previously been hot worked by about 10 per cent reduction between anneals. Rhys was successful in cold rolling 0.010-inch-thick strip, however, this material was very brittle. The ductility of the strip reduced to 0.02-inch thickness by hot working was superior to that of the thinner cold-rolled strip.

Arc-melted ruthenium was found to have poorer workability than the powder-metallurgy ruthenium; however, the arc-melted material of highest purity could be worked successfully to rod and strip.

The fabrication of osmium has received much less attention than ruthenium, and osmium is still considered unworkable. It seems, however, that techniques designed to produce ductile ruthenium would also be beneficial in the fabrication of osmium. The fabrication of osmium is further complicated by its volatile and toxic tetroxide which dictates that elevated-temperature working be done in an inert environment.

PHYSICAL PROPERTIES

The physical properties of the platinum-group metals have been summarized previously[1,3,7,11,12] and will not be discussed extensively here except where conflicting, or new data, have been uncovered. Physical-property data from several sources have been compared and where there is agreement the most extensive source is referenced. Where there is disagreement, several values are reported or the most widely accepted value is reported.

Atomic Number

Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
78	46	45	77	76	44

Atomic Weight

Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
195.23	106.7	102.91	193.1	190.2	101.7

Crystal Structure

Platinum, palladium, rhodium, and iridium all have face-centered-cubic structures; osmium and ruthenium have hexagonal close-packed structures. Early reports indicated the existence of two allotropic forms of rhodium and four allotropic forms of ruthenium.[7] Recent investigations by McCalden and Duwez[13] and Bale[14] reported no evidence of the allotropic transformations previously reported for rhodium and ruthenium.

Lattice Constants

The lattice constants of the platinum-group metals at 20 C are tabulated below:[7]

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
a, A	3.9258	3.8825	3.7957	3.8312	2.7304	2.6987
c, A	--	--	--	--	4.3104	4.2730

Density

Calculated and measured densities of the platinum metals at 20 C are tabulated below.[7] Both density values are reported. The measured density of osmium ranks it as the most dense element, although iridium has the higher calculated density.

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Measured, g/cm^3	21.4	11.9	12.4	22.4	22.5	12.2
Calculated, g/cm^3	21.4	12.02	12.4	22.65	22.61	12.45

Melting Point

The melting points of the platinum-group metals are tabulated below. It should be pointed out that the values of 2550 and 2750 C for ruthenium and osmium, respectively, that have been frequently reported are not included. More recent determinations[15] indicate that ruthenium melts at approximately 2250 C and osmium melts at approximately 3000 C.

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Melting Point, C	1769	1552	1960	2442	3000	2250

Boiling Point

The approximate boiling points of the platinum-group metals (with the exception of platinum) have been determined experimentally.[7] The boiling point of platinum was calculated from vapor-pressure data. In addition, values of the boiling points of these metals calculated by Brewer[16] are included.

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Boiling Point, C[7]	4530	3980	4500	5300	5500	4900
Boiling Point, Calculated, C[16]	4100	3440	4150	4800	4900	4500

It would be expected from vapor-pressure data and known melting points that the boiling point of rhodium would be higher than that of platinum, as is indicated by the data of Brewer.

Specific Heat

The specific heats of the platinum-group metals as functions of temperature are presented in Figure 2.[7] They are expressed analytically as follows:

	Specific Heat at 20 C, cal/g[12]	$C_p = a + bt - ct^2$ [7]
Platinum	0.032	$C_p = 0.031678 + 6.30574 \times 10^{-6} t - 1.67487 \times 10^{-6} t^2$ (to 1400 C)
Palladium	0.058	$C_p = 0.05841 + 1.5853 \times 10^{-5} t$ (to 1000 C)
Rhodium	0.059	$C_p = 0.060467 + 1.8303 \times 10^{-5} t$ (to 1000 C)
Iridium	0.032	$C_p = 0.030725 + 7.4004 \times 10^{-6} t$ (to 1700 C)
Osmium	0.031	$C_p = 0.030986 + 4.721 \times 10^{-6} t$ (to 1600 C)
Ruthenium	0.058	$C_p = 0.057439 + 1.8921 \times 10^{-5} t$ (to 1000 C)
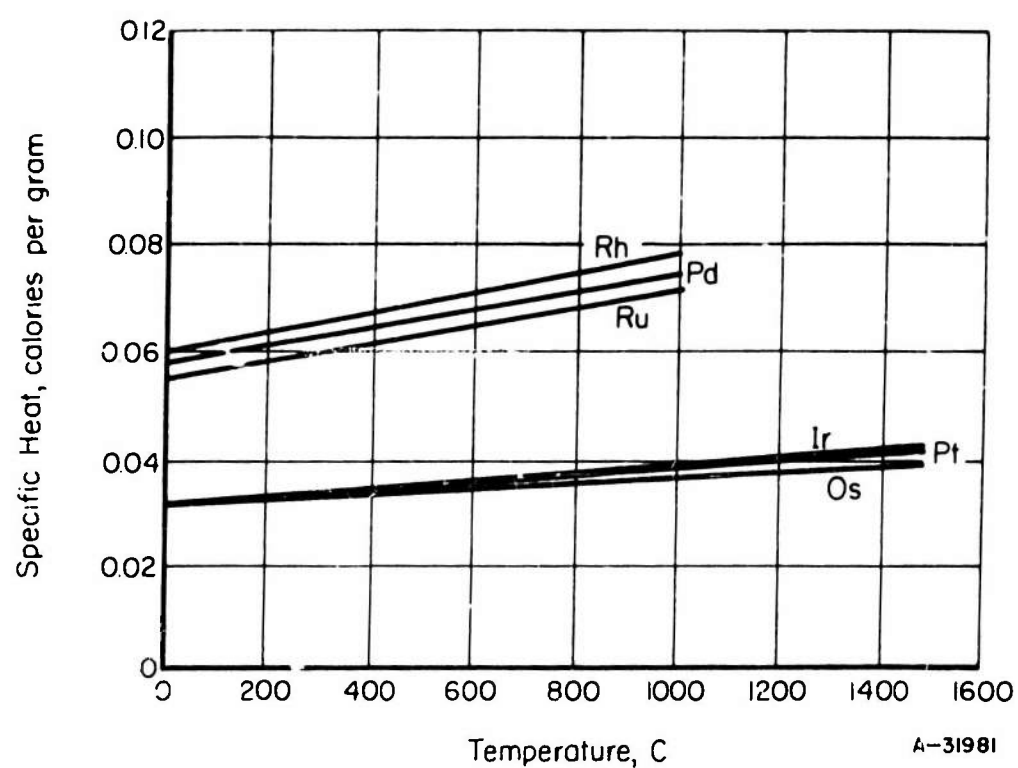
FIGURE 2. EFFECT OF TEMPERATURE ON THE SPECIFIC HEAT
OF THE PLATINUM METALS[7]

Thermal Conductivity

The thermal conductivities of the platinum metals at 20 C are tabulated below.[3,12]

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Thermal Conductivity, cal/(sec)(cm^2)(C/cm)	0.17	0.17	0.36	0.35	--	--

Thermal Expansion

The thermal expansion of platinum, palladium, rhodium, and iridium as a function of temperature is shown in Figure 3.[7] The coefficients of linear expansion between 0 to 100 C of all six metals are given below.[3,7,12]

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Coefficient of Linear Expansion, 10^{-6}/C	8.9	11.7	8.5	6.5	6.6	9.6

Vapor Pressure

The vapor-pressure data on the platinum-group metals have not been in general agreement. In some instances, the volatilization of the platinum metal oxides has been confused with volatilization of the metals, leading to erroneous conclusions as to the relative vapor pressure of the metals.

Some selected data from the work of Brewer[16] as tabulated by Dushman[17] are presented below. The temperatures, in C, necessary to achieve certain metal vapor pressures are given.

	Temperature, C, at Indicated Pressure, microns					
	10^{-2}	10^{-1}	1	10	100	1000
Platinum	1606	1744	1904	2090	2313	2582
Palladium	1156	1271	1405	1566	1759	2000
Rhodium	1681	1851	1971	2149	2358	2607
Iridium	1993	2154	2340	2556	2811	3118
Osmium	2101	2264	2451	2667	2920	3221
Ruthenium	1913	2058	2230	2431	2666	2946

These data, plus information from other sources, have been summarized with vapor-pressure data of the elements and their oxides and carbides from bromine to uranium by North American Aviation, Inc.[18] The data in this report are summarized graphically and will not be reproduced here.
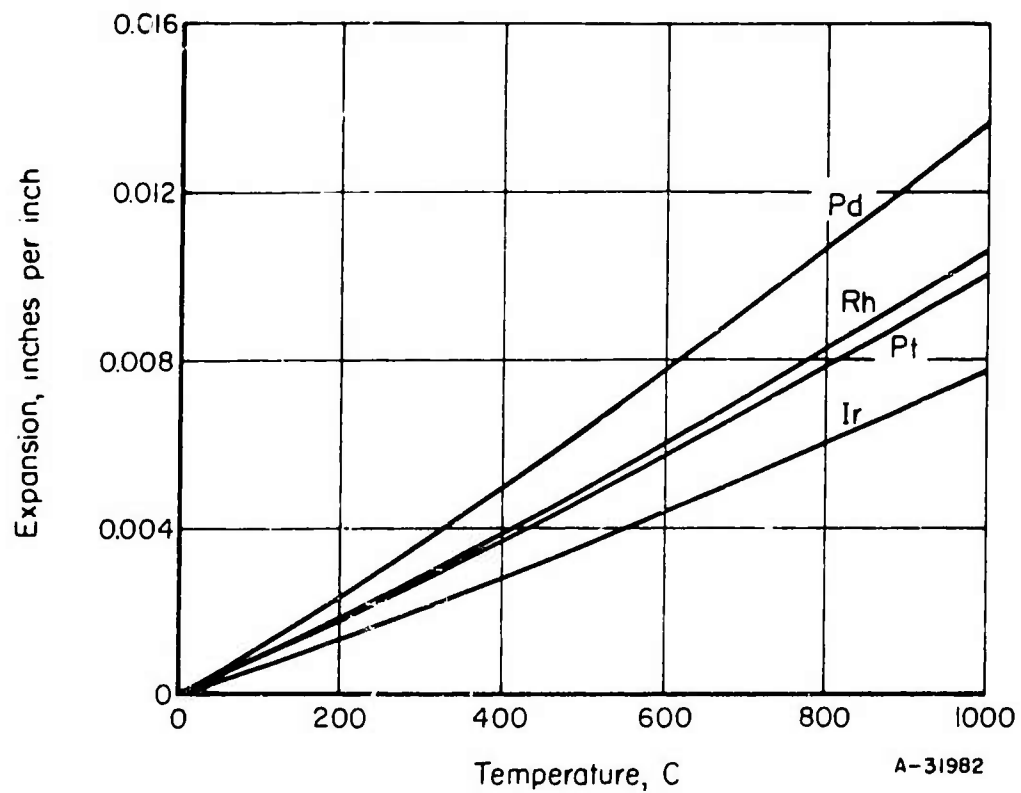
FIGURE 3. THERMAL EXPANSION OF THE PLATINUM METALS[7]

Haefling and Daane[18a] have recently determined the vapor pressure of palladium between 1115 and 1400 C. Their data fit the relationship $\log P_{mm} = \frac{16860 \pm 85}{T(K)} + 8.30 \pm 0.04$ which results in vapor pressures of a factor of almost 15 greater than previously recorded. This difference is felt to be due to increased accuracy of the measuring techniques.

Electrical Resistivity

The electrical resistivity of the metals at 20 C is presented below:[3]

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Electrical Resistivity, μohm-cm	10.6	10.7	4.7	5.3	9.5	(9.5)[3] (7.2)[7] (14.4)[1]

The effect of temperature on the resistivity of the four face-centered-cubic metals is shown in Figure 4.[7]

Emissivity

The effect of temperature on the emissivity of the platinum-group metals has not yet been thoroughly investigated. The available data from several sources are tabulated below:

Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium	Wavelength, λ, micron	References
0.30	0.33	0.24	0.30 (1750 C)	--	--	0.65(solid)	(7)
0.38	0.37	0.30	--	--	--	0.65(liquid)	(7)
0.30(1100 C)	0.35(1000 C)	--	--	--	--	0.66	(19)
0.30(1300 C)	0.31(1450 C)	--	--	--	--	0.66	(19)
0.31(1500 C)	0.37(1550 C)	--	--	-	--	0.66	(19)
0.37-0.11(total emissivity at 25-1500 C)							(3)

Magnetic Susceptibility

The magnetic susceptibilities of the platinum metals, except osmium, at various temperatures are tabulated on page 16.[7]

FIGURE 4. EFFECT OF TEMPERATURE ON THE ELECTRICAL RESISTIVITY
OF FOUR PLATINUM METALS[7]

Temperature, C	Magnetic Susceptibility, $\lambda \times 10^{-6}$, mass units				
	Platinum	Palladium	Rhodium	Iridium	Ruthenium
18	1.10	5.8	1.14	0.15	0.56
250	0.66	4.3	1.30	0.18	--
500	0.55	3.3	1.46	0.21	0.62
750	0.44	2.6	1.55	0.25	--
1000	0.36	2.1	1.80	0.29	0.70

Atomic Properties

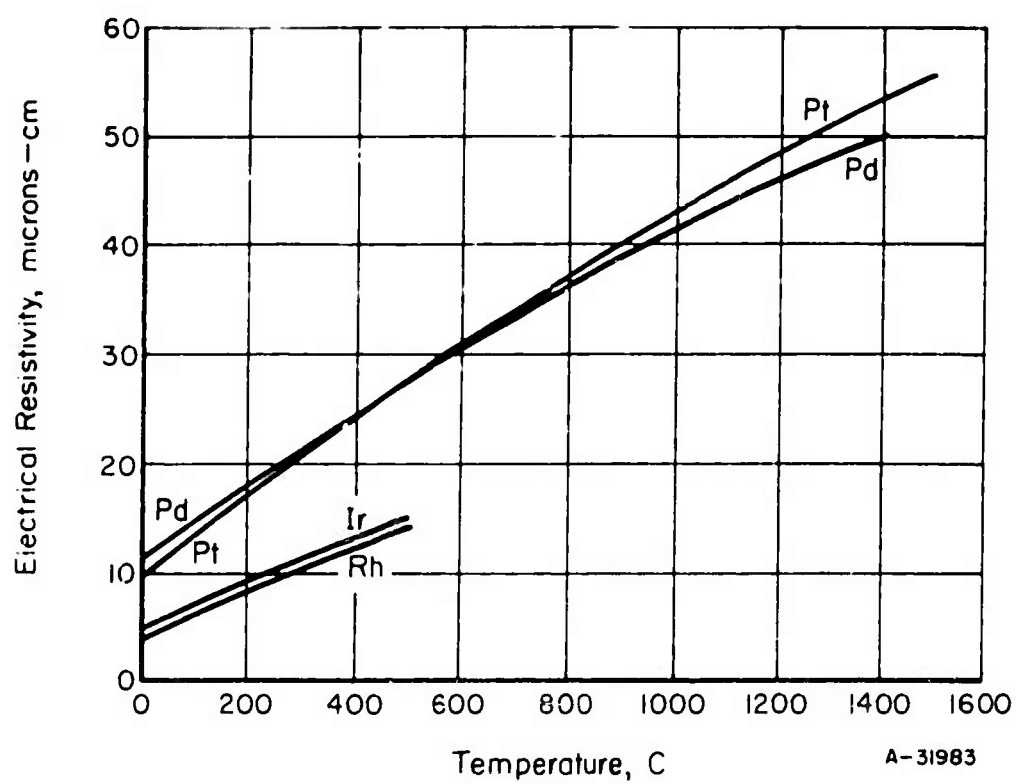In addition to some of the atomic and thermal properties listed previously, there are many other properties of the metal atoms that are of specialized interest. Some of these, such as atomic diameter, closest approach of atoms, ionization potential, chemical valence and valence electrons, atomic abundance in the earth's crust, the mass of the isotopes and the thermal-neutron-absorption cross section, are listed in Table 2.

TABLE 2. SOME ATOMIC PROPERTIES OF THE PLATINUM-GROUP METALS

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium	References
Atomic Diameter, kX	2.769	2.745	2.7	2.709	2.70	2.67	(20)
Distance of Closest Approach, kX	2.769	2.745	2.684	2.709	2.670	2.644	(20)
Ionization Potential, ev	8.96	8.33	7.7	8.7	8.7	7.5	(20)
Chemical Valence	4,2	2,4	3,4	4,6,8	4,6,8	3,4,6,8	(20)
Valence Electrons	$5d^26s^1$	$4d^{10}$	$4d^85s^1$	$5d^26s^2$	$5d^66s^2$	$4d^75s^1$	(20)
Atomic Abundance in Earth's Crust	4×10^{-8}	8×10^{-9}	1.6×10^{-9}	8×10^{-9}	4×10^{-8}	8×10^{-9}	(20)
Isotope Mass, A	192	102	103	191	184	96	(20)
	194	104	--	193	186	98	(20)
	195	105	--	--	187	99	(20)
	196	106	--	--	188	100	(20)
	198	108	--	--	189	101	(20)
	--	110	--	--	190	102	(20)
	--	--	--	--	192	104	(20)
Thermal-Neutron-Absorption Cross Section, barns/atom	8.1	8.0	150	430	14.7	2.46	(21)

Elastic Modulus

The more refractory platinum-group metals have among the highest known elastic moduli; osmium having a higher modulus than any other element.

The room-temperature values of elastic modulus of these metals are tabulated below.[3]

	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
Elastic Modulus, 10^6 psi	22	16	40	74	81	60
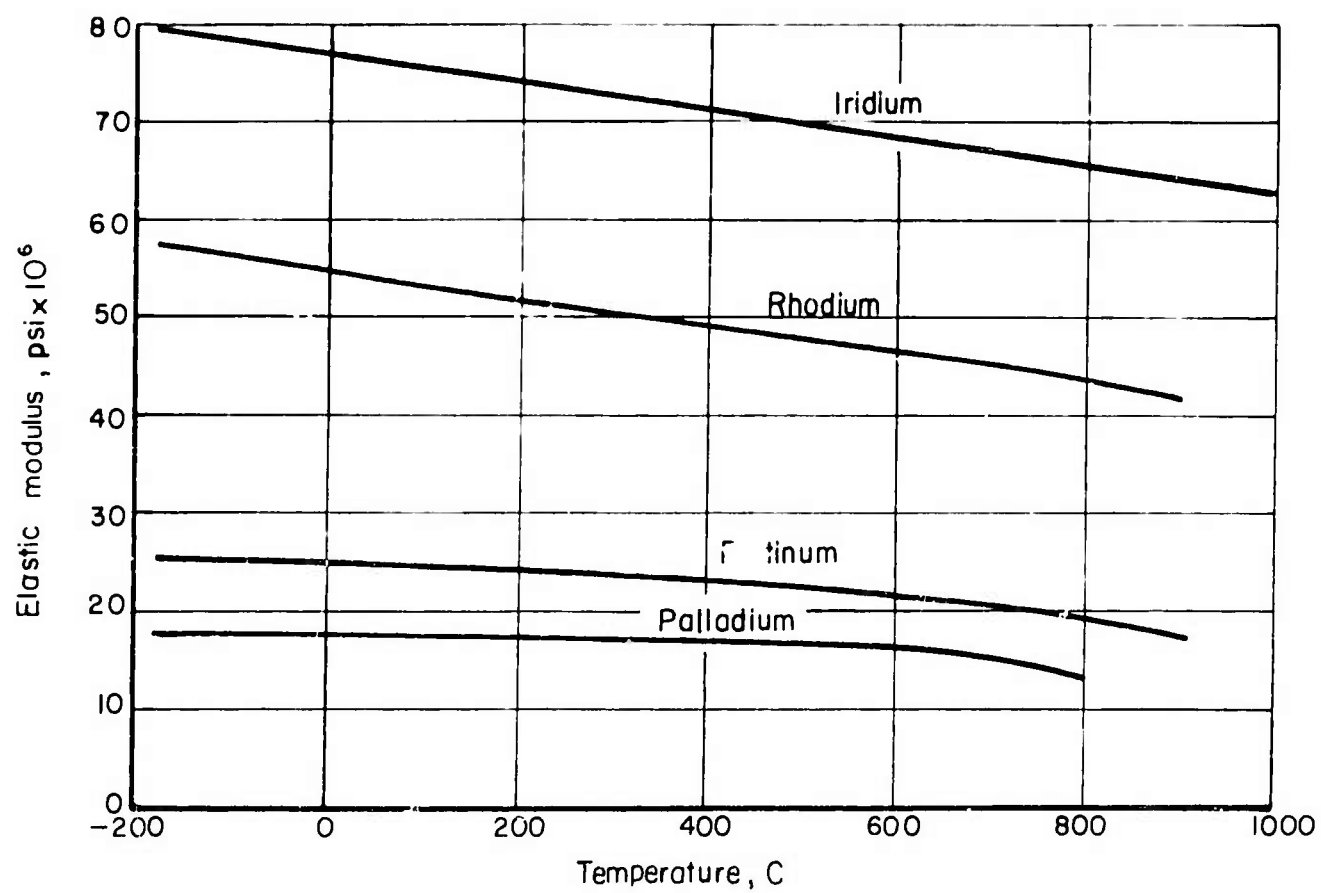
A-31984

FIGURE 5. EFFECT OF TEMPERATURE ON THE ELASTIC MODULUS
OF THE PLATINUM METALS[22]

The effect of temperature on the elastic modulus of the four face-centered-cubic metals, as reported by Köster[22], is shown in Figure 5. All of the modulus values at room temperature reported by Köster appear to be higher, especially for the case of rhodium, than those reported by others. This is probably because Köster reported dynamic modulus whereas the other values are representative of static modulus.

CHEMICAL PROPERTIES

Gas-Metal Reactions

Carbonaceous Gases

An interesting phenomenon has been observed with unstable hydrocarbons that crack in contact with hot platinum metals. Damage to the metals in the form of a fine intergranular precipitate of carbon extending some distance into the metal has been observed. No explanation is offered for this phenomenon.[23]

Most of the platinum-group metals are unaffected by exposure to commercial carbon monoxide; however, it has been observed that CO will harden palladium, and that ruthenium will react with CO to form a carbonyl at 180 C and very high pressures, of the order of 200 atmospheres.

Exposure to carbon dioxide reportedly has no effect on any of the platinum-group metals.[23]

Halogen Gases

Platinum. Investigations of the reaction of platinum with chlorine gas over the temperature range 500 to 800 C revealed the corrosion rate reaches a maximum at 570 C and then drops to a minimum, approximately one-fiftieth of the maximum at 650 C. This behavior is attributed to the change in vapor pressure and the nature of the platinum chloride reaction products.[23]

Studies by Nogareda[24] of the corrosion rate of platinum in chlorine and bromine gas at low pressures reveal that the corrosion rate varies with the second power of the gas pressure between 600 and 850 C, and with the first power of the pressure from 1200 to 1300 C.

The results of various studies indicate that up to 400 C a protective film, presumably $PtCl_2$ is formed; at 600 C no film is formed, and at 700 C a weight loss is observed. This is in disagreement with the first tests mentioned.

Hydrogen

Studies of the reactions of hydrogen with the platinum-group metals have largely centered on the palladium-hydrogen system. Of the other platinum-group metals, Smithells[19] reports only osmium and iridium do not adsorb hydrogen.

None of the platinum metals have been reported to be embrittled on exposure to hydrogen, however, exposure of palladium to oxygen and hydrogen atmospheres alternately does result in blistering from water vapor formation. This phenomenon also is common in copper and silver, but has not been observed in any of the other platinum-group metals.

A more complete presentation of the hydrogen-platinum metals systems is given later in the section "Alloy Systems".

Nitrogen

Smithells[19] reports that nitrogen is insoluble in all of the platinum-group metals.

There was no information found on the effect of nitrogen on the physical or mechanical properties of the metals.

Oxygen

Brewer[184] critically analyzed the available data for the oxides of the platinum-group metals. He concluded that many of the oxides have low decomposition temperatures, and their study must be carried out at temperatures where equilibrium conditions are difficult to obtain. Most of the work has been done without the aid of X-ray analysis, and many phases have been reported which do not exist. Many of the oxides have been prepared from aqueous solutions, and some of the reported oxide phases appear not to exist under anhydrous conditions.

The following decomposition temperatures (the temperature where the dissociation pressure of the solid oxide reaches 1 atmosphere of oxygen) have been given by Brewer:

Oxide	Decomposition Temperature, K	Oxide	Decomposition Temperature, K
PtO	780 ± 30	IrO_2	1373
Pt_3O_4	--		
PtO_2	750	RuO_2	1400 ± 30
		RuO_4	Metastable to $RuO_2 + O_2$
PdO	1150		
		OsO_2	Disproportionates at 923 K to
Rh_2O	1400		give 1 atm $OsO_4(g)$
RhO	1394		
Rh_2O_3	1150	OsO_4	Normal boiling point = 403

Based on these data, Brewer concluded that above about 1400 K (1127 C) no solid oxide phases can exist even in an atmosphere of oxygen. Using an argument based on thermodynamics, he concluded that, with the exception of osmium, only M_xO_2 and M_xO gaseous molecules can result from the reaction of oxygen with the platinum-group metals. M_xO_2 is supposed to be predominant at the lower temperatures, and M_xO should predominate at the higher temperatures where O_2 begins to dissociate appreciably into atomic oxygen.

Heats and free energies of formation, according to the compilation by Coughlin[282], are presented for several of the oxides of the platinum-group metals in Tables 3 and 4, respectively. Based on Coughlin's free-energy data, the decomposition temperatures for solid PdO, RhO, Rh_2O_3, IrO_2, and RuO_2 are 1160, 1300, 1215, 1030, and 1425 K, respectively.

Prior to presenting the experimental results concerning the behavior of the platinum-group metals in oxygen at elevated temperatures, a few of the problems associated with the interpretation of such data should be mentioned. The face-centered-cubic platinum-group metals are well known for their tarnish and oxidation resistance. Under many conditions of temperature and oxygen pressure they can be considered noble metals. All of the platinum-group metals have volatile oxides under certain temperature conditions. Throughout the literature there appears to be a question as to whether the metals vaporize and the oxides are formed from the vapor or whether a solid oxide is formed followed by immediate vaporization. Most investigators today agree that the latter is the case.

Because of the low oxidation rates exhibited by most of the platinum metals, the oxidation characteristics are extremely sensitive to impurities in the metal. In addition, since the oxides are volatile, it is possible to build up an oxide-metal equilibrium in a static atmosphere, thus leading to an erroneous picture of the oxidation characteristics. In a nonstagnant environment the flow rate of the oxidizing atmosphere could be expected to influence test results, especially with those metals with highly volatile oxides. Fryburg and Murphy[25] have commented on this effect and have reviewed some pertinent data to illustrate the effect of a moving versus a stagnant atmosphere. Because of the number of test variables, all of which have a large influence on experimental results, the following presentation will concentrate on the most extensive investigations where the variables mentioned will be assumed constant for all tests. In addition, comparisons of the results of several investigators will not be attempted unless there is a reasonable assurance that the experimental conditions are equivalent.

Platinum. Platinum is reported to form two oxides, PtO, produced by heating platinum sponge or platinum black in oxygen at 510 to 560 C[26], and PtO_2 which has been isolated and identified by Fryburg[27] as the volatile reaction product of platinum with activated oxygen. The formation of PtO_2 has also been noted by Güntherschulze and Betz[28] in an investigation of the oxidation of platinum in ionized gases. In addition, both of these oxides have been found coexisting in surface films on platinum electrodes.[29]

Schneider and Esch[30], in a study of the oxidation characteristics of platinum, report that the evaporation rate of platinum dioxide is strongly dependent upon oxygen pressure. Kubaschewski and Hopkins[31] conclude from Schneider's data that the

TABLE 3. HEATS OF FORMATION OF SEVERAL OF THE OXIDES OF THE PLATINUM-GROUP METALS

Temperature, K	Heat of Formation(a), kcal/mole							
	PdO	Rh_2O	RhO	Rh_2O_3	IrO_2	RuO_2	OsO_4 (Yellow, Liquid)	OsO_4 (White, Liquid)
298.16	-22.9	-22.5	-21.5	-63.5	-40.0	-56.5	-94.0	-92.5
400	-22.8	-22.5	-21.5	-67.5	-40.0	-56.0	-90.5	-90.5
500	-22.7	-22.0	-21.0	-67.0	-39.5	-56.0	--	--
600	-22.6	-21.5	-20.5	-66.5	-39.5	-55.5	--	--
700	-22.4	-21.5	-20.5	-66.0	-39.0	-55.0	--	--
800	-22.3	-21.0	-20.0	-65.5	-38.5	-55.0	--	--
900	-22.1	-20.5	-20.0	-65.0	-37.5	-54.5	--	--
1000	-21.9	-20.0	-19.5	-64.0	-36.5	-54.5	--	--
1100	-21.7	-20.0	-19.0	-63.5	-35.5	-54.0	--	--
1200	-21.4	-19.5	-19.0	-63.0	-34.5	-53.5	--	--
1300	-21.2	-19.0	-18.5	-62.5	-33.5	-53.5	--	--
1400	-20.9	-19.0	-18.0	-62.0	--	-53.0	--	--
1500	-20.6	-18.5	-18.0	-61.0	--	-53.0	--	--
1600	--	-18.0	--	--	--	--	--	--
1700	--	-18.0	--	--	--	--	--	--
1800	--	-17.5	--	--	--	--	--	--
1900	--	-17.0	--	--	--	--	--	--
2000	--	-16.5	--	--	--	--	--	--
Uncertainty	±2.0	±4.0	±4.0	±12.0	±6.0	±4.0	±5.0	±5.5

(a) Data apply to the crystalline state except for OsO_4; OsO_4 (yellow) melts at 323 K and boils at 403 K. OsO_4 (white) melts at 315 K and boils at 403 K.

TABLE 4. FREE ENERGIES OF FORMATION OF SEVERAL OF THE OXIDES OF THE PLATINUM-GROUP METALS

| Temperature, K	Free Energy of Formation(a), kcal/mole							
	PdO	Rh$_2$O	RhO	Rh$_2$O$_3$	IrO$_2$	RuO$_2$	OsO$_4$ (Yellow, Liquid)	OsO$_4$ (White, Liquid)
298.16	-16.8	-19.0	-16.0	-50.0	-28.0	-44.0	-71.5	-71.5
400	-14.7	-18.0	-14.0	-43.5	-24.0	-39.5	-64.5	-64.5
500	-12.7	-17.0	-12.5	-37.5	-20.0	-35.5	--	--
600	-10.7	-16.0	-10.5	-31.5	-16.0	-31.5	--	--
700	-8.7	-15.0	-9.0	-26.0	-12.0	-27.5	--	--
800	-6.8	-14.0	-7.5	-20.0	-8.5	-23.5	--	--
900	-4.8	-13.0	-6.0	-14.5	-4.5	-20.0	--	--
1000	-2.9	-12.5	-4.0	-9.0	-1.0	-16.0	--	--
1100	-1.1	-11.5	-2.5	-3.5	+2.5	-12.0	--	--
1200	±0.8	-11.0	-1.0	+2.0	+6.0	-8.5	--	--
1300	+2.6	-10.0	0.0	+7.0	+9.0	-4.5	--	--
1400	+4.5	-9.5	+1.5	+12.0	--	-1.0	--	--
1500	+6.3	-8.5	+3.0	+18.0	--	+3.0	--	--
1600	--	-8.0	--	--	--	--	--	--
1700	--	-7.5	--	--	--	--	--	--
1800	--	-7.0	--	--	--	--	--	--
1900	--	-6.0	--	--	--	--	--	--
2000	--	-5.5	--	--	--	--	--	--
Uncertainty	±2.0	±5.0	±4.5	±13.0	±6.0	±4.0	±5.5	±6.5

(a) Data apply to the crystalline state except for OsO$_4$; OsO$_4$ (yellow) melts at 329 K and boils at 403 K. OsO$_4$ (white) melts at 315 K and boils at 403 K.

pressure of the oxide increases in proportion to the oxygen pressure in agreement with the equilibrium relationship:

$$Pt + O_2(g) = PtO_2(g). \quad P_{PtO_2} = K/P_{O_2}. \quad K = 1.65 \times 10^{-6} \text{ at } 1200 \text{ C}.$$
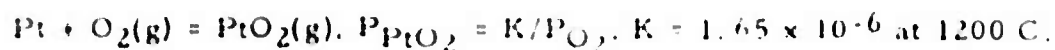
Several investigators[32, 33, 34, 35] have studied the oxidation of platinum in oxygen and flowing air at 1000 C and above.

The work of Raub and Plate[32] on the oxidation of platinum in oxygen is summarized in Figure 6. At 1000 and 1100 C the weight loss appears to be linear with time up to 30 hours' exposure. At 1200 and 1300 C, however, the rate of weight loss decreases with increasing time, the most significant departure from linearity being at 1200 C. The authors specified that the tests were carried out in flowing oxygen (0.4 liter/min), but the possibility exists that this flow was not sufficient to remove any stagnant environment which would result in an approach to an equilibrium of oxide vapor with metal. This explanation, however, does not account for the difference in the curves for the 1200 and 1300 C exposures.

The authors[32] also report that exposure to oxygen at 900 C resulted in weight losses of such a magnitude as to be measured on an analytical balance. However, work of other investigators[33, 34, 35] indicates that somewhere in the region of 900 C or below platinum should begin to show a weight gain. This would not be unexpected as the dissociation pressure of the platinum oxide would probably fall below 1 atmosphere of oxygen at some temperature. This is in agreement with Wöhler and Frey[36] who state that the dissociation pressure of PtO_2 at 530 C is under 592 mm of mercury.

The effect of alloying with other platinum-group metals on the oxidation resistance of platinum is shown in Figures 7 through 9.

The addition of palladium results in a slight increase in the weight loss as compared with pure platinum at 1100 C; however, the weight loss decreases with increasing palladium content up to 40 weight per cent palladium. This behavior can be attributed to increased oxygen solution resulting from the addition of palladium. At 1100 C the 40 per cent palladium alloy shows an initial increase in weight which later is eliminated by the volatilization of the oxide.

The effect of rhodium additions shown in Figure 8 can be divided into two separate effects. At 900 C, increasing the rhodium content results in a change from a weight loss at 10 weight per cent rhodium to a definite weight gain at 40 weight per cent rhodium, due to the formation of the trivalent rhodium oxide. At 1100 C the alloys show a decreasing weight loss with increasing rhodium concentration. The authors feel that an increase in the oxygen dissociation pressure of the oxide resulting from the alloying affinity between platinum and rhodium prevents the formation of the trivalent rhodium oxide in all of the alloys under investigation.

Additions of iridium, the least oxidation resistant of the face-centered-cubic platinum metals, result in increased weight loss of the platinum (see Figure 9). This effect is attributed to vaporization of the iridium plus an increased tendency toward volatilization of the platinum in the presence of iridium.
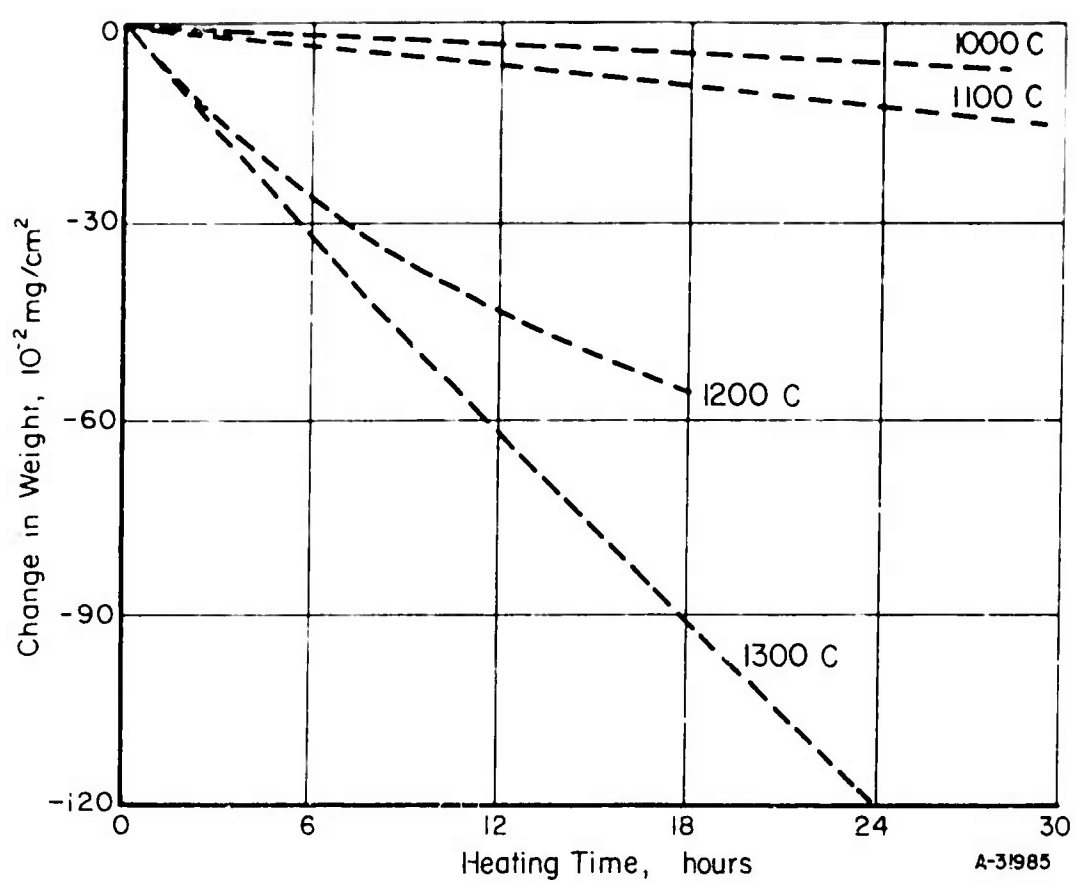
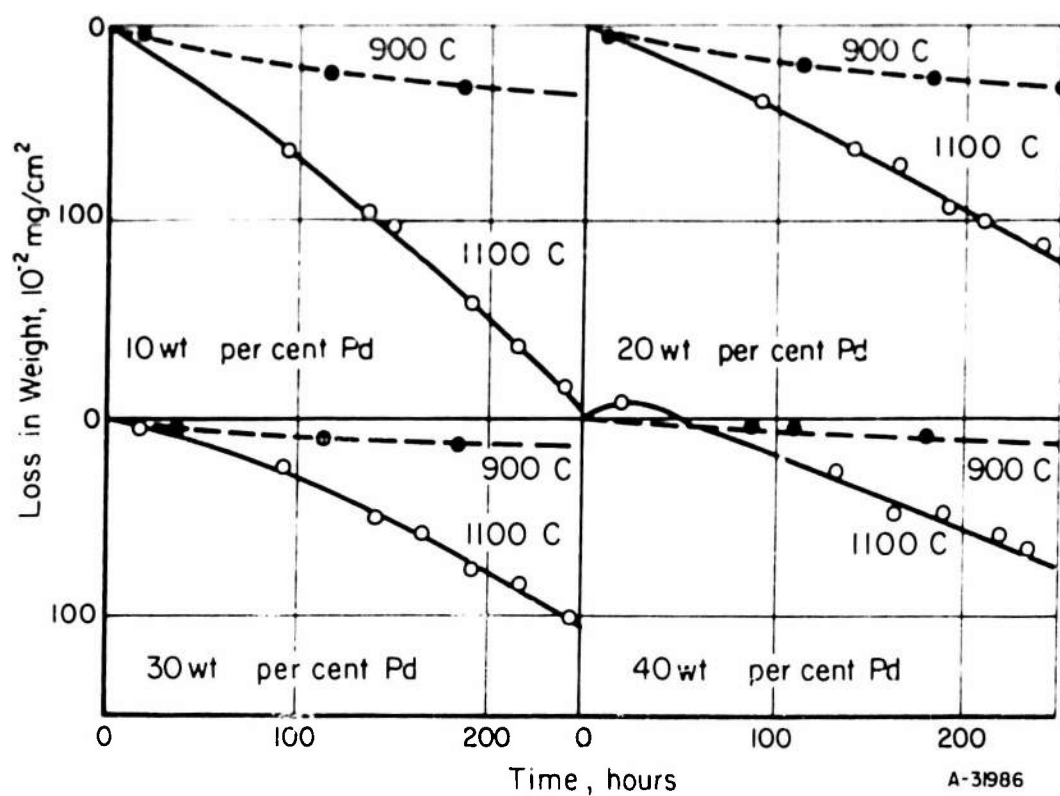FIGURE 6. CHANGES IN WEIGHT OF PLATINUM IN OXYGEN AT
VARIOUS TEMPERATURES[32]

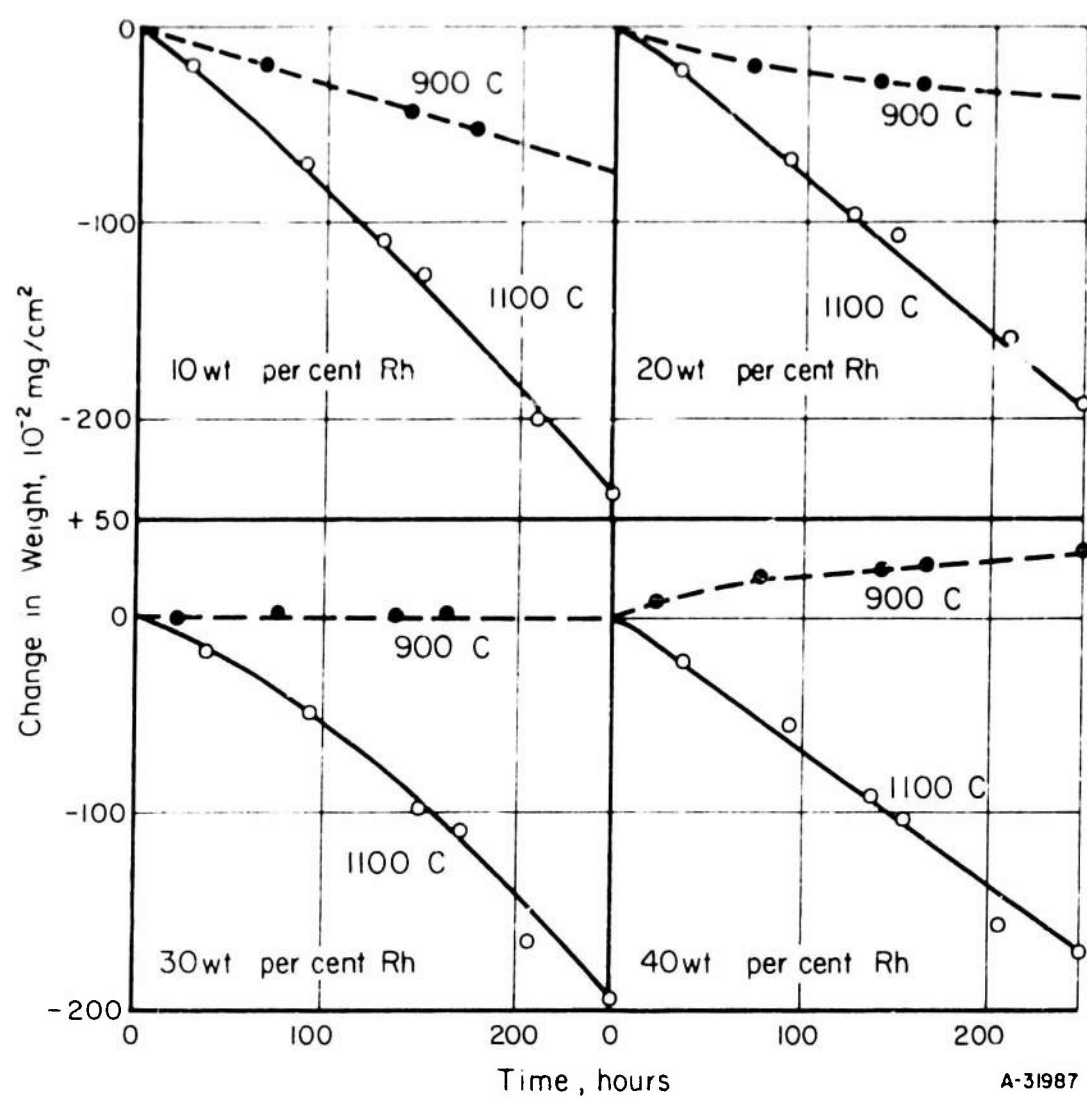FIGURE 7. TIME DEPENDENCY OF THE WEIGHT CHANGES OF PLATINUM-PALLADIUM ALLOYS IN OXYGEN AT 900 AND 1100 C[32]

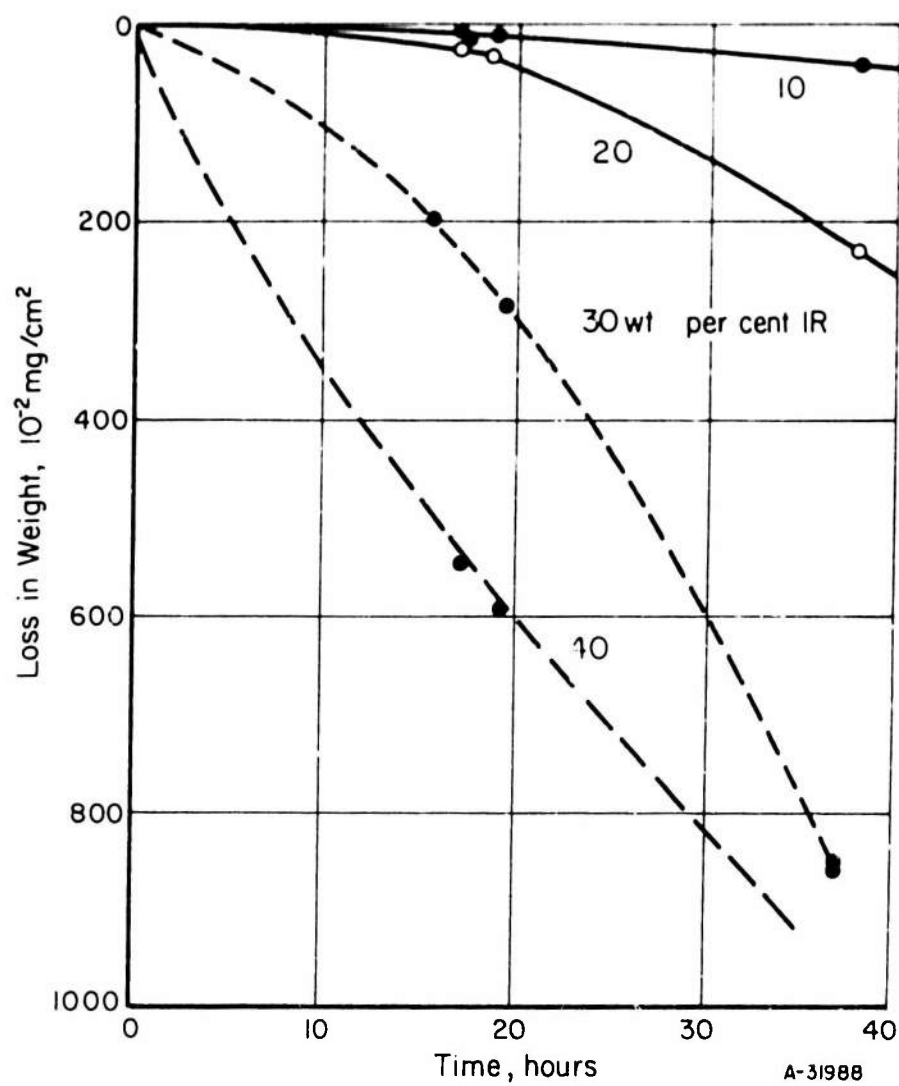FIGURE 8. TIME DEPENDENCY OF THE WEIGHT CHANGES OF PLATINUM-RHODIUM ALLOYS IN OXYGEN AT 900 AND 1100 C[32]

FIGURE 9. TIME DEPENDENCY OF THE WEIGHT LOSS OF PLATINUM-
IRIDIUM ALLOYS IN OXYGEN AT 900 C[32]

As a result of the volatilization of platinum oxide at elevated temperatures, platinum is susceptible to thermal etching. Lacroix[37] has reported thermal etching of platinum at 1000 C and above, and Raub and Plate[32] studied the thermal etching of platinum and platinum-palladium, platinum-rhodium, platinum-iridium, and platinum-gold alloys at various temperatures.

Palladium. Palladium when heated in an oxygen-containing atmosphere over a certain range of temperatures forms the bivalent palladium oxide, PdO, which subsequently dissociates at higher temperatures. In air, the oxide forms at temperatures from 350 to 790 C[38]. In environments richer in oxygen, this range would be extended to higher temperatures.

The work of Raub and Plate[32] is one of the most extensive studies of the high-temperature oxidation of palladium. A summary of their work on the oxidation characteristics of palladium is given in Figure 10. (All of the data shown in this figure are representative of specimens quenched from the testing temperature.) At all temperatures investigated, the palladium samples show an initial weight increase, the rate of weight gain increasing with increasing temperature. At 1100 C and above, the specimens show a weight loss following the initial increase in weight. This unusual behavior can be attributed to the interplay of two phenomena. The initial weight increase would be due to the solution of oxygen in the palladium lattice. Assuming the palladium did not combine with oxygen to any appreciable degree, the weight gain would stop as the oxygen content approached its saturation limit, as observed in the tests at 900 and 1000 C. However, the palladium does react with oxygen and subsequently volatilizes, thus giving rise to the weight loss observed at 1100 C and above.

The change in lattice parameter of palladium specimens heated in oxygen at temperatures from 800 to 1300 C and rapidly quenched also was studied. Using the parameter of a specimen annealed at 800 C in vacuum and quenched as base line, a definite decrease in parameter was noted in specimens annealed and quenched from higher temperatures. In addition, the structure of PdO was determined to be tetragonal with a = 3.03 kX and c/a = 1.754. The results of these investigations indicate that there is an appreciable solubility of oxygen in palladium that increases with increasing temperature.

Rhodium. Rhodium is the least volatile of the platinum metals.[39] It does, like palladium, form a tenacious oxide film at temperatures below 1000 to 1100 C, depending on the oxygen pressure of the environment.

Wöhler and Müller[40] have reported the existence of three rhodium oxides which have a dissociation pressure of 1 atmosphere of oxygen at 1113, 1121, and 1127 C for the trivalent, bivalent, and monovalent rhodium oxides, respectively. Brewer[184] reported that the only definitely determined phase is Rh_2O_3 (corundum structure). He questioned the interpretation of Wöhler and Müller on the grounds that their data do not distinguish between distinct phases and an extended homogeneity range. Kubaschewski and Catterall[185] concluded from the available data that Rh_2O_3 is the only stable oxide at room temperature and that Rh_2O and RhO are metastable.
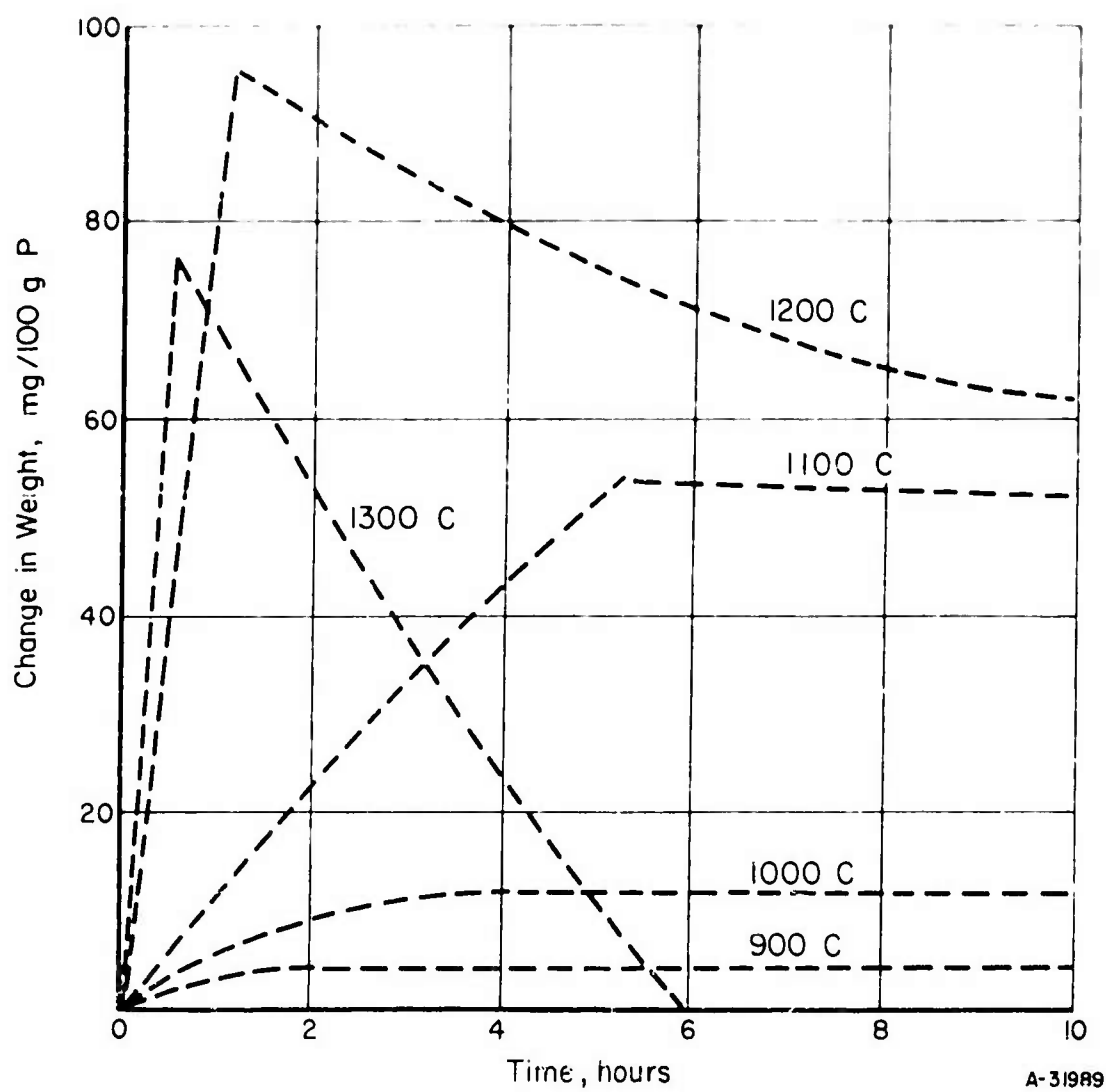
FIGURE 10.   CHANGES IN WEIGHT OF PALLADIUM IN OXYGEN
AT VARIOUS TEMPERATURES[32]

Raub and Plate[32] have studied the high-temperature oxidation characteristics of rhodium at 1100, 1200, and 1300 C. The results of their work are summarized in Figure 11. Rhodium, like palladium exhibits a weight gain at 1100 C, most of which is due to oxygen solubility. At 1200 C there is a very slight initial weight gain that is soon overcome by the volatilization of the oxide, leading to an approximately linear weight loss with time. At 1300 C, the volatilization is so rapid that any weight increase due to oxygen in solution is hidden. However, the rhodium specimen after being heated in vacuum, following 9 hours in oxygen at 1300 C, exhibited a weight loss of 0.02 mg/dm^2 or 1.56 mg/100 g of rhodium, thus indicating an appreciable oxygen solubility at 1300 C.

Iridium. IrO$_2$ appears to be the only stable oxide in the iridium-oxygen system. Goldschmidt[182] reports this to be of the same type as TiO$_2$ (C4 type) with a = 4.50 A and c/a = 0.700.

Iridium is considered the least oxidation resistant of the face-centered-cubic platinum-group metals. It oxidizes slowly upon exposure to air at 600 to 1000 C; however, above 1000 C the oxide, IrO$_2$, is quite volatile.[7,23]

There have been very few investigations of the oxidation characteristics of iridium; recently, due to the emphasis on protection of molybdenum, some properties of electroplated iridium have been studied.

Table 5 is a summary of the short-time exposure characteristics of plated iridium.[41]

TABLE 5. SHORT-TIME EXPOSURE CHARACTERISTICS OF ELECTROPLATED IRIDIUM[41]

| Material | Change in Weight in Air, mg/in.^{2} | | | | | |
| | 600 C | | | 1000 C | | |
	10 Min	20 Min	30 Min	10 Min	20 Min	30 Min
410 stainless steel, bare	-0.25	-0.53	-0.52	+1.14	+3.73	+14.5
410 stainless steel, iridium plated, 0.0005 in. thick	+0.06	+0.08	+0.11	+33.2	+36.7	+40.0
Molybdenum, bare	+0.32	+3.7	+4.0	-317.3	-596.5	(a)
Molybdenum, iridium plated, 0.0005 in. thick	+0.3	+0.3	+0.3	+0.31	+0.09	-0.42

(a) Sample completely disintegrated.

The data here do not appear compatible when the molybdenum and stainless steel results are compared. It appears from the results on molybdenum that the iridium plating afforded good protection and that the oxidation data are perhaps representative of only iridium. It would appear from the data at 1000 C that the iridium, like rhodium and palladium, has a definite oxygen solubility which is masked after long exposure by the weight loss resulting from the volatilization of IrO$_2$.
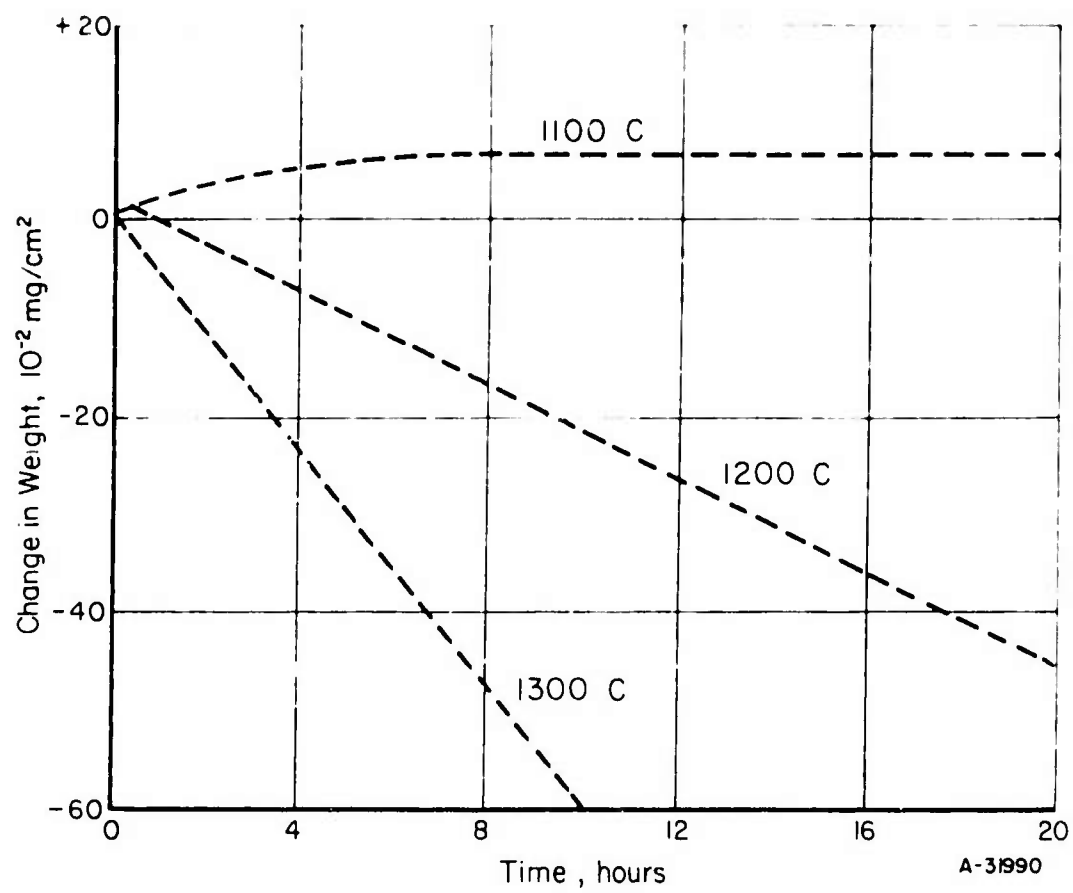
FIGURE 11. CHANGES IN WEIGHT OF RHODIUM IN OXYGEN AT
VARIOUS TEMPERATURES[32]

Ruthenium. Ruthenium commonly forms two oxides, RuO_2 and RuO_4. RuO_2 is the reaction product of ruthenium in oxygen at temperatures up to 960 C.[23] Like IrO_2, RuO_2 is volatile only at high temperatures. In the region of 600 C a measurable oxide film is formed, the thickness of the film increasing with increasing time at temperature.[42] The higher oxide of ruthenium has been isolated as a product of certain wet chemical reactions, but there was no definite evidence found in the literature that RuO_4 is formed on heating in air. Brewer[184] concluded that RuO_4 appears to be thermodynamically unstable even at room temperature.

Ruthenium is considered to follow iridium in order of decreasing oxidation resistance, although very few data are available and no systematic studies have been reported on the oxidation characteristics of this metal.

Osmium. OsO_2 (rutile structure) and OsO_4 are the only known oxides of osmium.[184] The yellow tetroxide is the stable form, melting at 56 C and boiling at 130 C under atmospheric pressure. OsO_4 also has a white form which is metastable with respect to the yellow form.

Osmium has the most volatile oxide of all the platinum-group metals. No data are available other than that the toxic osmium tetroxide vaporizes at 130 C in air.[73]

Sulfurous Gases

Platinum. Platinum, used in the manufacture of H_2SO_4, is unattacked after exposure to a mixture of SO_2, air, and SO_3 at 400 to 450 C. In SO_2 alone after 1 hour at 800 C there is no attack; however, after 1 hour at 1000 C a weight loss of 0.0013 g/cm^2 is reported. There also is a reaction in H_2S from 400 to 1000 C which produces a slight blue film, but no loss in ductility is observed after exposure.[23]

Palladium. Exposure of palladium to SO_2 at 800 and 1000 C reportedly results in etching at 1000 C and the formation of a purple-blue film, which is heavier at 1000 than at 800 C. No loss in ductility was observed at either temperature. Heating in H_2S above 600 C resulted in rapid attack through the formation of a low-melting sulfide eutectic.[23]

Corrosion by Liquid Media

The platinum-group metals are among the most corrosion-resistant elements known. In many corrosive environments rhodium, iridium, and ruthenium are completely resistant to chemical attack.[23] Table 6 is a compilation of the corrosion resistance of all the platinum metals in a number of common corrosive environments. Table 7 summarizes the corrosion behavior of the platinum metals except osmium in a number of fused salts.

TABLE 6. CORROSION OF THE PLATINUM-GROUP METALS IN A NUMBER OF COMMON CORROSIVE ENVIRONMENTS[23]

Corrosive Medium	Temperature, C	Platinum	Palladium	Rhodium	Iridium	Osmium	Ruthenium
H_2SO_4, conc.	RT	A	A	A	A	A	A
	100	A	C	B	A	A	A
H_2SeO_4, sp gr 1.4	RT	A	C	--	--	--	•
	100	C	D	--	--	--	--
H_3PO_4	100	A	B	A	A	D	A
$HClO_4$	RT	A	A	--	--	--	--
	100	A	C	--	--	--	--
HNO_3, 70%	RT	A	D	A	--	C	A
HNO_3, 95%	RT	A	D	A	A	D	A
	100	A	D	A	A	D	A
Aqua regia	RT	D	D	A	A	D	A
	Boiling	D	D	A	A	D	A
HF, 40%	RT	A	A	A	A	A	A
HCl, 36%	RT	A	A	A	A	A	A
	100	B	B	A	A	C	A
HBr, sp gr 1.7	RT	B	D	B	A	A	A
	100	D	D	C	A	C	A
HI, sp gr 1.75	RT	A	D	A	A	B	A
	100	D	--	A	A	C	A
Acetic acid, glacial	100	A	A	A	A	--	A
F_2	RT	B	--	--	--	--	--
Cl_2, dry	RT	B	C	A	A	A	A
Cl_2, moist	RT	B	D	A	A	C	A
Br (liq), dry	RT	C	D	A	A	D	A
Br (liq), moist	RT	C	D	A	A	B	A
Br, water	RT	A	B	A	A	--	A
I, dry	RT	A	A	A	A	B	A
I, moist	RT	A	B	B	A	A	A
I, in alcohol	RT	A	B	B	A	--	A
H_2S, moist	RT	A	A	A	A	A	A
NaClO solution	RT	A	C	B	--	D	D
	100	A	D	B	B	D	D
KCN solution	RT	A	C	--	--	--	--
	100	C	D	--	--	--	--
$HgCl_2$ solution	100	A	A	A	A	--	C
$CuCl_2$ solution	100	A	B	--	--	--	--
$CuSO_4$ solution	100	A	A	A	A	--	A
$Al_2(SO_4)_3$ solution	100	A	A	A	A	--	A

Note:

A - no appreciable corrosion

B - some attack but not enough to preclude use

C - attacked enough to preclude use

D - rapid attack.

Test on massive specimens, except for Os; solutions not aerated or stirred.

TABLE 7. CORROSION OF THE PLATINUM-GROUP METALS IN FUSED SALTS(23)

Corrosive	Temperature, C	Weight Loss After 1-Hr Exposure, mg/dm/day				
		Platinum	Palladium	Rhodium	Iridium	Ruthenium
KHSO$_4$	440	72.0	432.0	1,320	36	505
KCN	700	28,000	32,000	11,000	1,800	1,680
NaCN	700	7,450	14,200	25,200	4,800	3,600
1KCN + 2NaCN	550	840	8,160	24,500	2,160	2,160
KNO$_3$	350	0.0	0.0	36	72	1,200
NaNO$_3$	350	0.0	0.0	120	3.6	264
NaOH (reducing cond.)	350	--	192	180	3.6	720
Na$_2$O$_2$	350	0.0	360	336	72.0	33,600
Na$_2$CO$_3$ (reducing cond.)	920	72	108	-48	-132	-890
HCl, moist	540	0.0	--	--	--	--
		(4 hr)				
HCl + carbon	750	0.0	--	--	--	--

METALLURGICAL PROPERTIES

Mechanical Properties of the Pure Metals

Few data on the mechanical properties of the platinum-group metals are available. Little is known of the effects of various testing variables (strain rate, prior strain, stress system, temperature, etc.) on the properties of any of these materials. Platinum and palladium have received the most attention with respect to tensile properties; rhodium and iridium have received little attention, and no data have been reported for ruthenium and osmium.

Room-Temperature Properties

The available room-temperature tensile properties are summarized in Table 8, and the room-temperature hardness data of the metals in various metallurgical conditions are summarized in Table 9. Where data are in agreement, the values have been averaged and the references cited; where there appears to be wide variations in data, the values of each investigator are reported individually.

The well-known softness and ductility of platinum and palladium are shown by the relatively low strengths and high elongations of these materials in the annealed condition. Rhodium and iridium, on the other hand, have higher tensile strengths and considerably lower ductilities. It may be noted from the tensile data for rhodium and iridium that some values reported for the annealed and worked conditions are conspicuously high. The values of 138,000-psi tensile strength with a corresponding elongation of 35 per cent[3] for rhodium are not in agreement with data from other sources.[12, 14] Unfortunately, the purity of the rhodium and the iridium which exhibited these unusually high strength levels is not specified, whereas the other tensile data are representative of high-purity material.

Although the work-hardening characteristics of the four face-centered-cubic metals have not been thoroughly investigated, some insight into their behavior can be gained from a comparison of the various tensile properties. Platinum and palladium cold rolled 50 per cent exhibit increases of 1.5 and 2.0 times the annealed strength, respectively. On the other hand, rhodium and iridium exhibit strength increases of a factor of 3 on cold working by an unspecified amount. It is doubtful that, even under the most favorable conditions of purity and prior fabrication, rhodium and iridium could be rolled to a 50 per cent reduction to be comparable to the platinum and palladium. In fact, the maximum possible reduction between anneals probably would be of the order of 10 to 20 per cent.

Although rhodium and iridium are notoriously difficult to work, very little has been done to study this behavior, especially through the determination of mechanical properties. Bale[14] attempted to explain the difficulty of working rhodium by testing rhodium of extremely high purity, less than 10 ppm metallic impurities. This material exhibited a threefold increase in hardness after cold rolling 15 per cent. He concluded that although high-purity annealed rhodium is rather soft, its rate of work hardening, like that of rhenium, is extremely rapid at room temperature; this might indicate an

TABLE 8. ROOM-TEMPERATURE TENSILE PROPERTIES OF THE PLATINUM-GROUP METALS

Metal	Condition	Ultimate Tensile Strength, 1000 psi	0.2% Offset Yield Stress, 1000 psi	Proportional Limit, 1000 psi	Elongation, per cent	References
Platinum	Annealed	18-21	12	2-4	40	(1), (7), (11), (12), (43), (44)
	Cold rolled, 50%	28-30	--	--	3.5	(1), (7)
Palladium	Annealed	20-28	7-8	5	24-40	(1), (7), (11), (12), (44), (46)
	Cold rolled, 50%	47	--	32	1.5	(7), (11)
Rhodium	Annealed	67	--	--	6.5	(14)
		48	--	--	5.7	(12)
		138	--	--	35	(3)
	Cold worked	365	--	--	2	(3)
Iridium	Annealed	32	--	--	--	(12), (15)
		80	--	--	9	(3)
	Cold worked	290	--	--	6	(3)
Ruthenium	Rolled and annealed strip	55	--	--	5	(10a)
Osmium	The tensile properties of osmium have not been determined					

TABLE 9. ROOM-TEMPERATURE HARDNESS OF THE PLATINUM-GROUP METALS

Metal	Condition	Vickers Hardness Number	References
Platinum	Wrought-annealed	37	(7)
	Cast-annealed	55	(46)
	Electrodeposited from complex sodium platinate bath	606-642	(47)
Palladium	Wrought-annealed	37	(7)
	Cast-annealed	48	(46)
	Electrodeposited from palladosamine bath	190-196	(48)
	Electrodeposited from metal nitrates plus chlorides bath	387-435	(48)
Rhodium	Pressed and sintered plus 3 hours at 1300 C	135	(46)
	The above plus 1.5 hours at 1600 C	128	(46)
	Wrought-annealed at 1200 C	122	(49)
	Vacuum annealed, high purity	110	(14)
	Cold rolled, 15 per cent	300	(14)
	Electrodeposited from rhodium sulfate bath	549-641	(47)
	Cast	139	(11)
Iridium	Pressed and sintered plus 3 hours at 1300 C	270	(46)
	The above plus 1.5 hours at 2000 C	178	(46)
	Cast	163-172 Bhn	(50), (51)
	Cast	217 Bhn	(52)
	Vacuum-arc melted-annealed	210-240	(15)
Osmium	Vacuum-arc melted; hardness variation due to different crystallographic orientations of grains	300-670	(53)
	High purity-cast	350	(7)
	Cold worked, 7 per cent	690-1000 Avg ~710	(15)
Ruthenium	Vacuum-arc melted	200-500	(15)
	Cast	220 Bhn	(11)
	Cast-annealed	240	(12)
	Cold worked, 9 per cent	360-750 Avg ~480	(15)

operative slip mechanism different from that found in other face-centered-cubic metals. The possibility exists, in the case of both rhodium and iridium, that they are extremely sensitive to oxygen or some other dissolved interstitial.

Very little is known about the effect of temperature on the ductility of these metals. There is no evidence that the platinum or palladium undergoes a ductile-brittle transition. It is known that iridium wire can be bent slowly, but rapid bending may result in fracture. This gives a crude indication that the material is strain-rate sensitive, and that the ductile-brittle transition in bending is close to room temperature.

Rhys[10a] reports that single crystals of ruthenium produced by zone melting are quite ductile and can be bent easily by hand, and that hot-rolled annealed strip can be bent to an angle of 90 deg over a 1-inch radius. Cold-rolled and annealed ruthenium strip is considerably less ductile and fractures at lower amounts of plastic deformation.

Very little is known regarding the operative deformation systems in these metals. It can be safely assumed that platinum and palladium, like most face-centered-cubic metals, slip on the $\{111\}$ planes in the $<110>$ direction. There are no data to indicate the operative slip systems in rhodium and iridium.

Ruthenium and osmium, like many other hexagonal materials, slip on the $\{10\overline{1}0\}$ planes and also, in the case of osmium, in the basal, (0001), plane. Ruthenium is reported to have several operative twinning planes, the $\{10\overline{1}1\}$, $\{11\overline{2}1\}$ $\{11\overline{2}3\}$, and occasionally the $\{10\overline{1}2\}$. In this respect it is very much like rhenium, zirconium, and titanium. Osmium, like many of the more common hexagonal materials, twins on the $\{10\overline{1}2\}$ and $\{10\overline{1}1\}$ planes.[54] There are no data available on the twinning planes of platinum, palladium, rhodium, and iridium; however, they probably twin on the $\{111\}$ planes as do most other face-centered-cubic metals.

Elevated-Temperature Properties

The elevated-temperature hardness of all of the metals has been investigated and a summary of these data is presented in Figures 12 and 13. The hardness of the more refractory metals is unusually high at temperatures above 1000 C, the average hardness of ruthenium and osmium at 1200 C being about 125 and 300 VHN, respectively. The hardness of rhodium and iridium at 1100 C is significant y high in view of the high purity of these materials.

The tensile properties of palladium and platinum up to 1100 and 1200 C, respectively, are presented in Figure 14. The strength decrease of palladium with temperature appears to be almost linear, whereas the hardness-temperature curve changes slope rather abruptly at about 400 and 800 C. The effect of temperature on the tensile strength and hardness of platinum is very similar at the higher temperatures, but at low temperatures there is no plateau in the tensile-strength curve.

The creep properties of the platinum-group metals are virtually unknown. Platinum has been subjected to several investigations, especially in recent years, but palladium, rhodium, and iridium have received very little attention. Allen and Carrington[56] have investigated the compression-creep properties of several refractory metals, among them platinum, palladium, rhodium, and iridium. Some of the
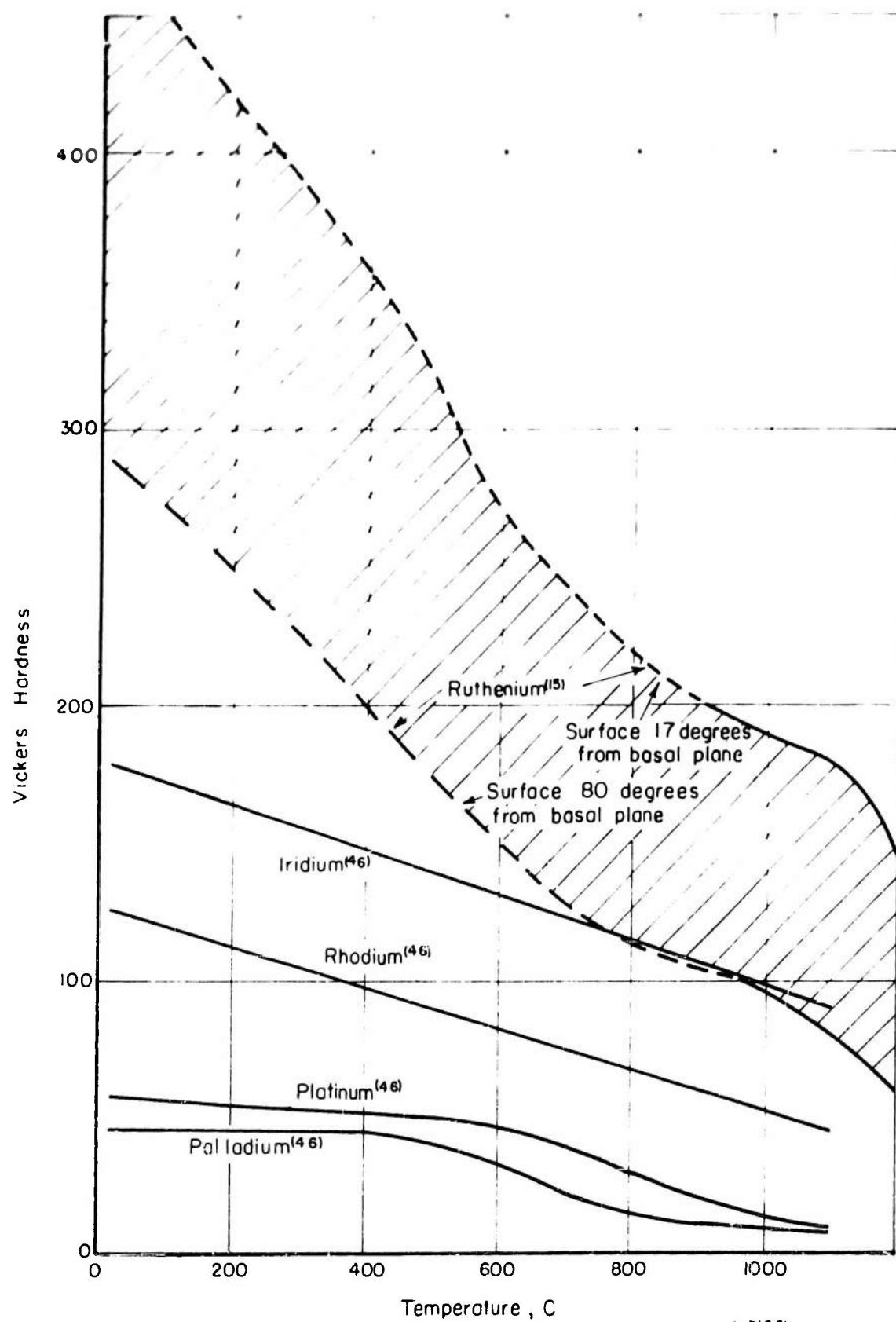
FIGURE 12. EFFECT OF TEMPERATURE ON THE HARDNESS OF PLATINUM,
PALLADIUM, RHODIUM, IRIDIUM, AND RUTHENIUM

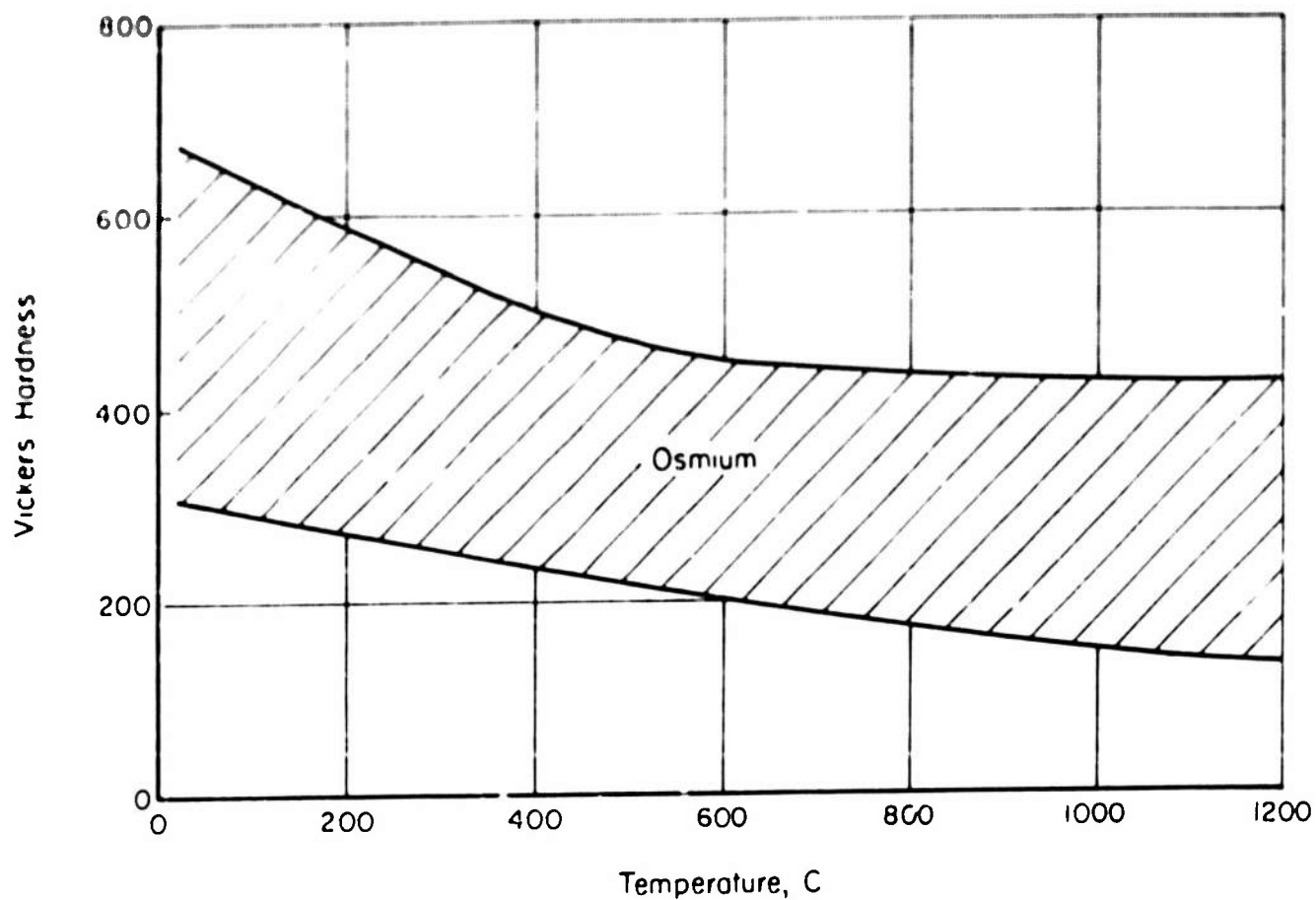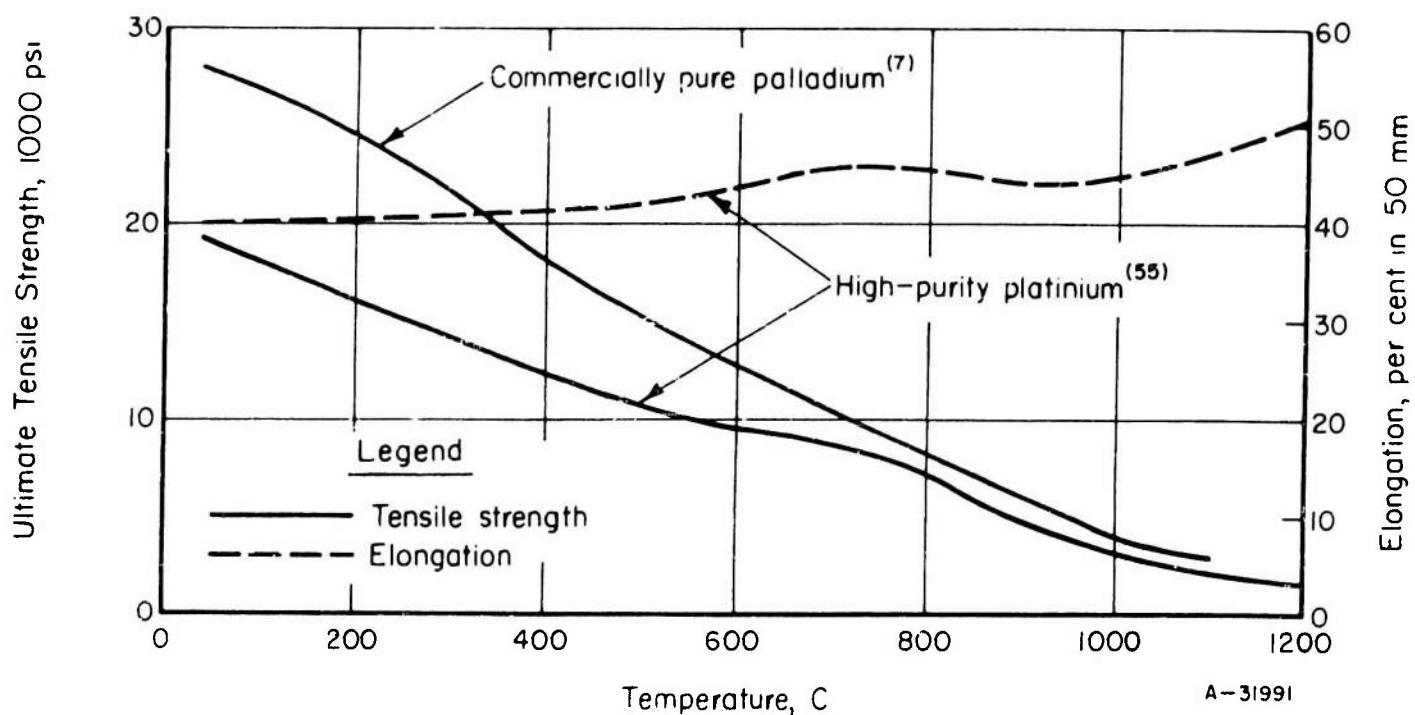FIGURE 13. EFFECT OF TEMPERATURE ON THE HARDNESS OF OSMIUM[15]

FIGURE 14. EFFECT OF TEMPERATURE ON THE TENSILE PROPERTIES
OF PLATINUM AND PALLADIUM

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results of their study, showing the stress and stress-density ratio to produce 1 per cent deformation in 24 hours at 1000 C in the platinum metals and molybdenum, tungsten, and iron, are tabulated below:

Material	Stress for 1% Deformation in 24 Hr at 1000 C, psi	Stress/Density x 10^{4}
Platinum	200	0.029
Palladium	660	0.154
Rhodium	6,600	1.49
Iridium	13,200	1.64
Molybdenum	6600-8800	1.81-2.41
Tungsten	13,200	1.90
Iron	1,057	0.375

It is seen that, although platinum and palladium are inferior to the other materials with regard to creep strength, rhodium and iridium compare favorably with molybdenum and tungsten, and are far superior to iron on a strength-weight basis.

The creep and stress-rupture data on platinum and palladium that are available have been generated by many sources with many different objectives, so that a concise correlation of the work of various investigators is rather difficult.

Reinacher[55] determined the 20-hour rupture strength of high-purity platinum over a range of temperatures from 20 to 1250 C. He found that the ratio of 20-hour rupture strength to short-time tensile strength decreases with increasing testing temperature, indicating that the short-time tensile strength is a poor design criterion for elevated-temperature applications. The values reported by Reinacher are listed in Table 10.

TABLE 10. ELEVATED-TEMPERATURE MECHANICAL PROPERTIES OF HIGH-PURITY PLATINUM[55]

Temperature, C	Ultimate Tensile Strength, 1000 psi	Stress to Rupture in 20 Hr, 1000 psi	Ratio of 20-Hr Rupture to Ultimate Strength
20	19.2	17.9	0.93
300	14.2	12.4	0.88
500	10.9	8.5	0.78
700	9.2	5.0	0.54
900	4.8	2.1	0.45
1250	1.4	0.85	0.60

Some stress-rupture properties of platinum have been determined by Child[57], Stauss[58], and Bennett[6]. The results of the studies of these investigators are summarized below.

Material	Temperature, C	\multicolumn{4}{c}{Stress to Rupture, psi}	References

Material	Temperature, C	1 Hr	10 Hr	100 Hr	1000 Hr	References
Platinum	900	--	--	3630	1650	(57)
99.97% platinum, 1200 C annealed, 0.010-in.-diameter wire	1100	1875	1250	625	600	(58)
Annealed 0.020-in.-diameter wire	1400	250	120	--	--	(6)

Stauss also observed that exposures greater than 5 hours' duration resulted in a change in the fracture characteristics from the usual necking-type fracture to a knife-edge type of fracture. Metallographic investigation revealed that grain growth during exposure resulted in single crystals across the specimen diameter. Bennett also noted such grain growth during exposure under low stress levels; however, in this case the grain growth resulted in embrittlement.

Other investigations of the creep characteristics of platinum have followed different lines. Carrecker[59], in a study of the plastic flow of metals as a function of temperature and amount and rate of deformation, investigated the creep behavior of platinum wire at several temperatures and stress levels. His data yielded some relatively straightforward relations between stress, σ, strain, ϵ, strain rate, $\dot{\epsilon}$, and absolute temperature, T. These relationships are listed below.

$$(1) \quad = A\dot{\epsilon}^n]_{\epsilon, T}; \quad (2) \quad \sigma = Be^{pT}]_{\epsilon, \dot{\epsilon}}$$

$$(3) \quad \epsilon = Ct^a]_{\sigma, T}; \quad (4) \quad \frac{\partial n}{\partial T} = \frac{\partial p}{\partial \log \dot{\epsilon}}]_\epsilon$$

$$(5) \quad Q \propto \log \sigma]_\epsilon$$

where Q = activation energy for rate of deformation, t = time, and A, B, C, a, n, and p are constants.

The effect of stress and temperature on the strain rate at a constant stress of 0.01 is shown in Figure 15. From these data the constants A, n, B, and p, in Equations (1) and (2) can be calculated. The data concerning the time dependency of strain are too voluminous to be presented here.

Only two studies of the creep properties of palladium are known. Atkinson and Furman[60] studied the creep behavior of platinum, platinum-10 rhodium, and palladium (deoxidized with calcium boride, CaB_6, and aluminum) at 750 C under relatively
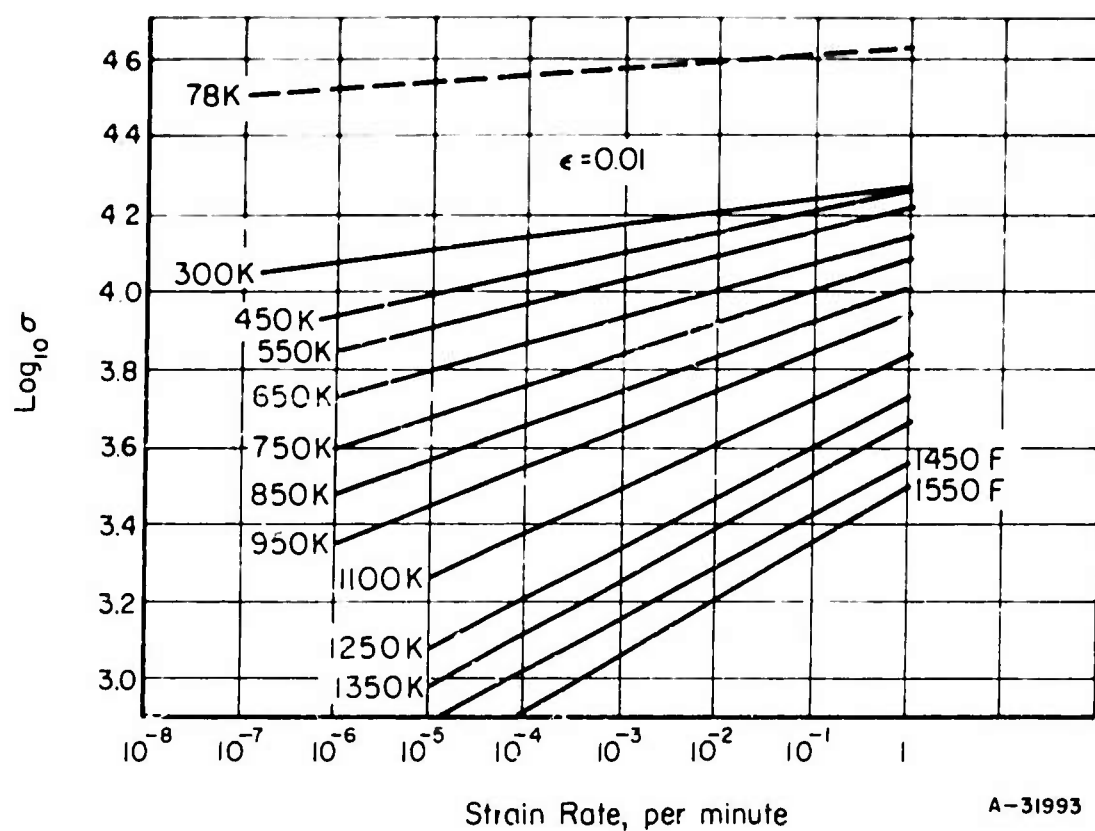
FIGURE 15. STRAIN RATE IN PLATINUM WIRES AT A STRAIN OF 0.01
AS A FUNCTION OF STRESS AT SEVERAL TEMPERATURES

low stress levels for very long times. The results of these tests, showing the creep rate after 1000, 2000, and 3000-hour exposures are given in Table 11.

TABLE 11 CREEP BEHAVIOR OF PLATINUM, PLATINUM-10 RHODIUM, AND PALLADIUM AT 730 C

Material	Annealing Temperature, C	Average Grain Diameter, inch	Stress, psi	Creep Rate, 10^{-5} %/hr			Length of Test, hr	Estimated Stress for Creep Rate of 10^{-5} %/Hr, psi
				1000 Hr	2000 Hr	3000 Hr		
Platinum	750	0.004	250	0.04	0.08	0.04	3817	
	750	0.004	250	0.03	0.03	..	2929	
	750	0.004	400	0.33	0.26	.	2256	270
Platinum-10 rhodium	750	0.0021	400	0.40	0.40	.	2153	
	1050	0.0032	400	0.17	0.13	..	2107	
	1050	0.0032	550	0.38	0.22	..	2135	340
Palladium + CaB_6	750	0.015	250	1.43	0.19	0.04	3090	
Palladium + CaB_6	750	0.015	150	0.56	0.08	0.02	3017	
Palladium + aluminum	750	0.015	250	0.67	0.18	0.05	3119	440
Palladium + aluminum	750[a]	0.015	250	0.09	0.03	0.02	3032	

(a) Annealed for 1200 hours prior to loading.

The data for the platinum-10 rhodium alloy are presented here to point out the effect of grain size on the creep rate at these low stress levels. The platinum-10 rhodium alloy would be expected to have better creep resistance than pure platinum; however, the alloy specimen with the smallest grain size is markedly inferior to platinum and to the alloy specimens of larger grain size.

The data presented for palladium are significant in view of the high rate of first-stage creep that is observed in comparison with platinum, followed by a marked decrease in creep rate at 2000 and 3000 hours.

Microscopic examination of the test specimens revealed intergranular attack, and subscale formation extending to a considerable depth below the surface. A specimen annealed for 1200 hours to form the subscale prior to testing showed significantly reduced creep rates. The authors seem to imply that the high first-stage creep resulted from this reaction during the initial 1000 hours of testing; it seems more reasonable to assume that the subscale formation is the cause of the improvement in the creep rates at 2000 and 3000 hours, and that palladium inherently has a high first-stage creep rate.

Albert and Sadowski[3] have determined the stress-rupture properties of commercial platinum and palladium and several alloys at 927 C. Their data, presented in Table 12, indicate that platinum is far superior to palladium with regard to rupture life. This marked superiority of platinum over palladium is not readily apparent from the creep-rate data of Atkinson and Furman, although there is no sound basis for comparison between the two investigations.

TABLE 12. STRESS-RUPTURE PROPERTIES OF COMMERCIALLY PURE PLATINUM AND PALLADIUM AT 927 C IN AIR[3]

Material	Stress, psi	Rupture Life, hours	Elongation, per cent in 1.3 in.	Reduction in Area, per cent
Platinum	2000	58.2	98.6	91.2
	1500	355.6	92.5	99.6
	1250	1020.7	79.0 (approx.)	--
Palladium	2000	0.7	96.6	Formed point
	1000	13.7	56.2	Ditto
	500	322.2	6.2	4.3

The abrupt loss in ductility of palladium during exposure under the 500-psi stress suggests that the intergranular attack and subscale formation observed by Atkinson and Furman may be a factor in the apparently anomalous results for palladium.

Recrystallization and Cold Work

Because of the limited data available, it is difficult to compare the platinum-group metals on the basis of their work-hardening and recrystallization characteristics. There are desultory data in the literature on the annealing and recrystallization of palladium, rhodium, and iridium which may be summarized as follows:

Rhodium will recrystallize at 800 C (per cent work unspecified)[7]

Pure palladium has a VHN of 37 after annealing at 800 C (softest condition reported[7]

Commercial palladium has an average VHN of 46 after annealing at 800 C and about 44 VHN after annealing at 1000 or 1100 C[7]

Iridium has been completely softened by annealing at 2000 C.[7]

One of the definitive works on the recrystallization of the platinum metals is that of Wise and Vines[61] who determined the recrystallization temperatures of Grade 2 platinum (99.99 per cent) for various degrees of cold work (0 to 89 per cent). The data obtained from their work are summarized in Table 13.

TABLE 13. EFFECT OF COLD WORK ON THE HARDNESS AND
RECRYSTALLIZATION TEMPERATURE OF
GRADE 2 PLATINUM[61]

Reduction, per cent	Vickers Hardness Number	Recrystallization Temperature, C[a]
19	72	765
39.5	85	700
50.8	92	635
66	101	600
80.5	114	545
89.5	122	425

(a) All specimens annealed for 15 minutes.

This work was performed on platinum with an estimated purity of 99.99+ per cent in order to eliminate the effects of impurities from the results. It was found that neither increases in the annealing time nor in the annealing temperature had any appreciable effect on the recrystallized grain size, but that the grain size was an inverse function of the amount of cold work; i.e., the greater the amount of cold work, the smaller the recrystallized grain size.

In this same experiment, the work-hardening behavior of platinum was demonstrated by a rapid increase in hardness up to 10 to 15 per cent reduction in thickness, a more gradual increase between 15 and 75 per cent reduction, and then a slightly more rapid increase from 75 to 90 per cent reduction. The rate of work hardening (increase in hardness/per cent reduction) was found to decrease rapidly up to 30 or 40 per cent reduction, increase gradually up to 70 or 80 per cent reduction, and then increase rapidly from 80 per cent on.

The effect of annealing time on the recrystallization process in platinum for various temperatures and reductions is illustrated in Table 14.

Although these data are incomplete in the sense that the only isothermal curves of hardness versus annealing time which could be drawn are those for 400 C, there is evidence of a decreasing activation energy for recrystallization with increasing per cent reduction. The rapidity with which the recrystallization process occurs once it has been initiated is not immediately apparent from the data, since there is no clear dividing line between recovery and recrystallization in the case of those specimens which have not reached the hardness of fully recrystallized material. There does, however, seem to be an increase in the rate of recrystallization with increasing per cent reduction.

Another paper of importance on the recrystallization of platinum is that of Middleton, Pfeil, and Rhodes[8] on the recrystallization of platinum produced by powder-metallurgical techniques. As shown in the curves of Figures 16 and 17, the recrystallization temperature of platinum produced by this method is dependent on the

TABLE 14. ANNEALING-HARDNESS TESTS ON PURE PLATINUM(61)

Reduction, per cent	Vickers Hardness, As Rolled	Vickers Hardness After Annealing for Time and at Temperature Indicated												
		1/4 Hr, 300 C	1 Hr, 300 C	1/4 Hr, 400 C	1 Hr, 400 C	48 Hr, 400 C	96 Hr, 400 C	1/4 Hr, 500 C	1/4 Hr, 600 C	1/4 Hr, 700 C	1/4 Hr, 800 C	1/4 Hr, 900 C	1/4 Hr, 1000 C	1/4 Hr, 1100 C
19	72.4	70	70.2	69.0	68.2	68.0	69.7	67.4	68.9	52.7	39.7	39.4	37.9	37.4
39.5	85.6	84.7	84.2	83.4	80.2	78.6	73.9	81.4	63.3	40.0	34.3	38.1	38.1	38.5
50.8	91.9	89.7	91.4	85.4	86.8	78.6	72.6	83.4	48.1	38.9	39.4	39.4	38.3	38.6
66	102	97.1	98.4	94.9	91.7	51.5	49.7	76.2	41.2	39.3	39.9	39.9	34.6	39.4
80.5	113	111	109	92.8	61.0	40.8	--	57.0	39.5	39.7	39.6	40.0	40.2	38.1
89.5	124	114	--	54.2	42.5	40.0	40.1	41.0	39.8	39.9	39.6	40.2	41.8	..
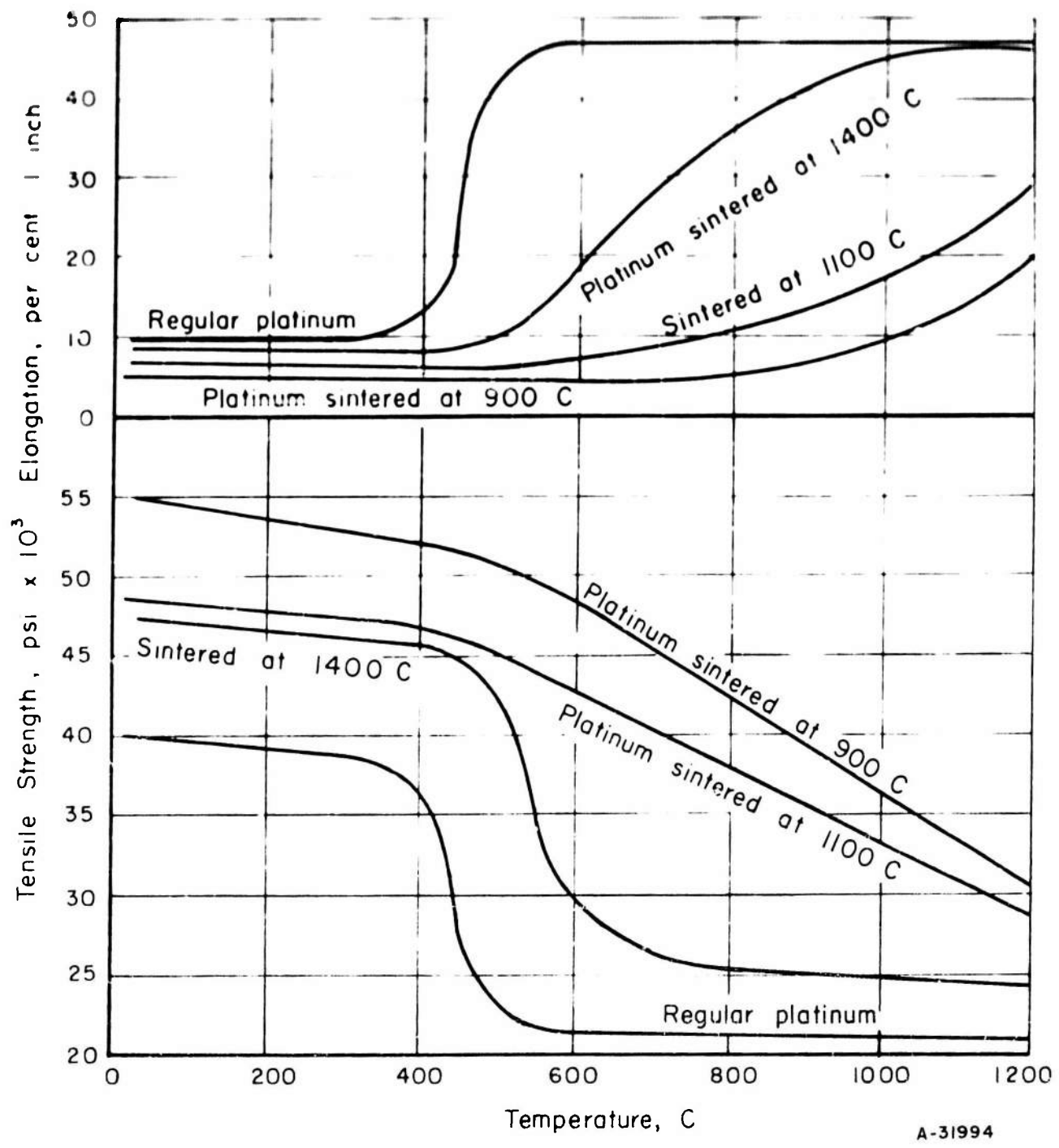
FIGURE 16. EFFECT OF HEATING FOR 15 MINUTES ON THE TENSILE
STRENGTH AND ELONGATION OF 92 PER CENT COLD-
DRAWN PLATINUM WIRES PRODUCED UNDER
VARIOUS CONDITIONS[8]
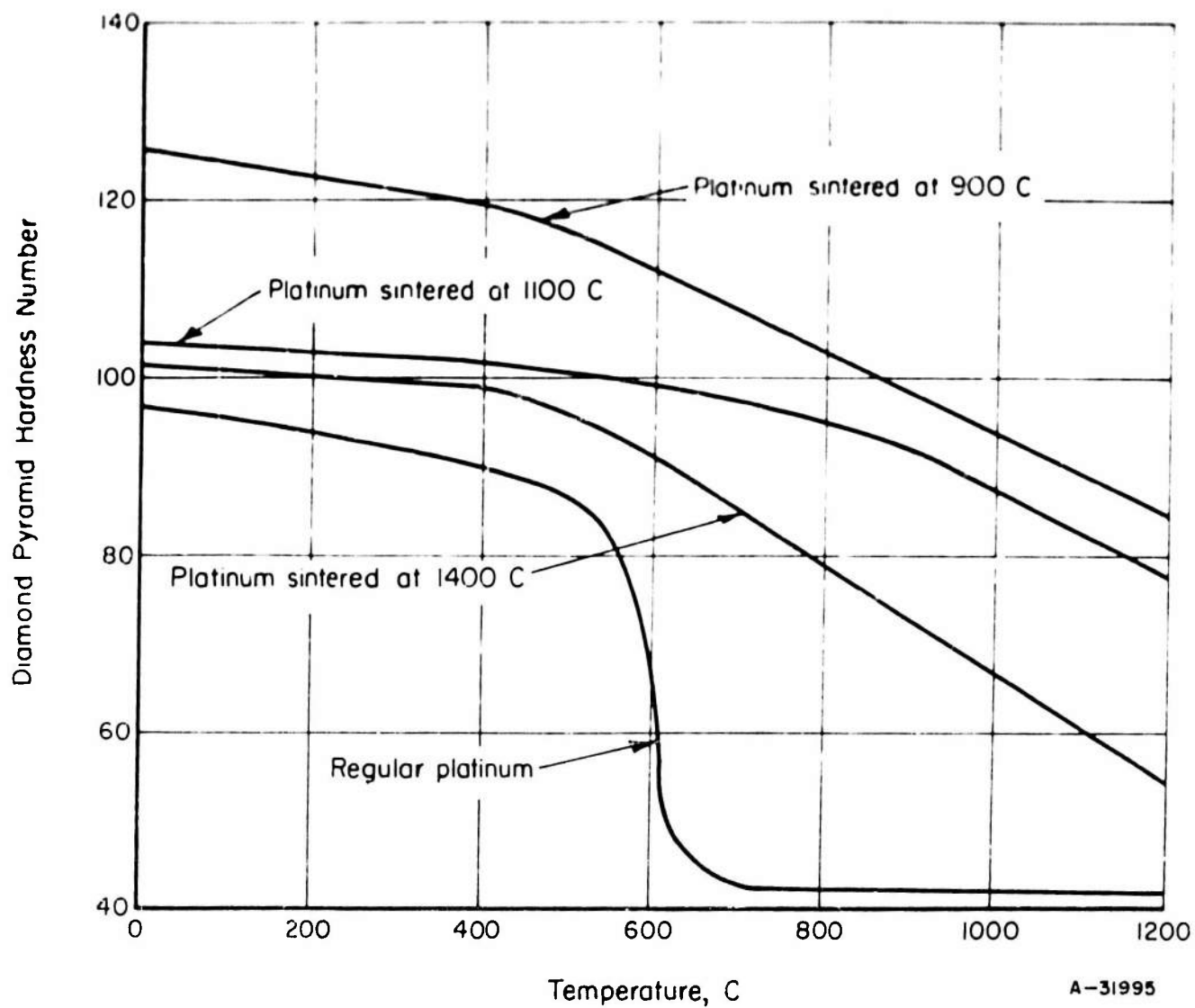
FIGURE 17. EFFECT OF HEATING FOR 15 MINUTES ON THE HARDNESS
OF 92 PER CENT COLD-DRAWN PLATINUM WIRES
PRODUCED UNDER VARIOUS CONDITIONS[8]

sintering temperature and deviates markedly from the curves for regular platinum. It is suggested by the authors that the high recrystallization temperature of the sintered platinum is due to suitably dispersed porosity. The purity of the material used in this experiment was 99.9+ per cent platinum.

Alloy Systems

This section includes the available information on the constitution of binary alloys of the platinum-group metals. The emphasis here is on systems involving rhodium, iridium, osmium, and ruthenium, and constitution diagrams of systems involving these elements are presented wherever available. The constitution diagrams of platinum- and palladium-base alloys have been omitted, mainly because of the large number that are available and published in other reviews.[5,7] In the following discussions, when an alloy system is omitted (for instance, silver-osmium) it is because no information has been found concerning that system.

A particularly valuable reference work for information on alloy systems is Hansen and Anderko's Constitution of Binary Alloys. (See "Bibliography" at end of text.) Many of the data presented here were condensed from this book, however, sufficient new references are included that it was considered necessary to include all of the data in this report.

Silver

Iridium. Iridium is reported to be insoluble in molten silver.[62]

Palladium. Several investigators[7,63,64,65] conclude that silver and palladium form a continuous series of solid solutions. However, Theirer[66], on the basis of discontinuities in the thermal expansion, and Glander[67], on the basis of studies of the system silver-copper-palladium, conclude that new phases form in the solid state.

Platinum. The solubility of silver in platinum is reportedly between 7.5 and 13.25 weight per cent (13.5 and 22.5 atomic per cent) silver.[68]

Two intermediate homogeneity ranges having ordered structures with ideal compositions PtAg (face-centered cubic) and Pt_3Ag (face-centered cubic) exist below 750 C.[69,70] The ordered Pt_3Ag undergoes a transformation to another ordered structure below 650 C.

Rhodium. Rhodium, like iridium, is reportedly insoluble in molten silver.[62] However, X-ray investigations of silver-rhodium alloys show that these alloys consist of practically pure silver and a rhodium solid solution of at most 0.07 weight per cent (0.1 atomic per cent) silver.[71]

Ruthenium. Investigation of a 5 weight per cent (2.4 atomic per cent) ruthenium alloy indicates some slight solid solubility of ruthenium in silver.[72]

Aluminum

Palladium. Grube and Jauch[73] have studied the palladium-aluminum system using thermal, thermoresistometric, and metallographic studies of several alloys. Their phase relationships show a solubility of approximately 4.1 weight per cent (15 atomic per cent) aluminum in palladium at 400 C and the existence of three compound phases, $PdAl_3$, $PdAl$, and Pd_2Al, corresponding to the compositions 43.14, 20.19, and 11.22 weight per cent aluminum, respectively.

Platinum. According to Chouriguine[74], there appears to be no solid solubility of platinum in aluminum. Investigation of alloys containing up to 80 weight per cent (35.6 atomic per cent) platinum shows three phases forming from hypereutectic melts. The phase richest in platinum probably is $PtAl_3$ (70.69 weight per cent platinum).

Arsenic

The compounds MAs_2 have been reported for all of the platinum-group metals except osmium. All of these compounds can be made by synthesis of the elements; however, for the more refractory metals, heating the metal trichloride with arsenic in a hydrogen stream is perhaps the easiest way of obtaining the compound.[75]

Gold

Iridium. The solid solubility of iridium in gold is reportedly negligibly small.[76] No investigations into the solid solubility of gold in iridium have been reported.

Osmium. Linde[76] has shown by electrical-resistance methods that osmium, like iridium, has negligible solid solubility in gold.

Palladium. Studies by Ruer[77] established that palladium and gold form a continuous series of solid solutions. The results of other investigations[78,79,80] of physical properties of the palladium-gold system support this conclusion; however, some peculiarities in curves of thermal emf[81] and electrical resistivity[82] versus composition in the neighborhood of 70 weight per cent gold indicate the possibility of a structural change in this region.

Platinum. Darling, Mintern, and Chuston[83] have studied the phase relationships of the platinum-gold system and shown the existence of a two-phase region,

ranging from about 1.75 to 81 weight per cent (2 to 81 atomic per cent) gold at 600 C, with a maximum temperature of approximately 1250 C at 40 weight per cent (40 atomic per cent) gold.

Rhodium. Microscopic and X-ray studies show that the rhodium-gold system consists of terminal solid solutions of 2.2 to 4.9 weight per cent (4.1 to 9.0 atomic per cent) rhodium in gold, and 2 to 4.5 weight per cent (1.1 to 2.4 atomic per cent) gold in rhodium with no intermediate phases existing.[62,71]

Linde[76] has reported that the solid solubility of rhodium in gold is about 0.3 weight per cent (0.56 atomic per cent) at 900 C.

Ruthenium. Linde[76] has shown by electrical-resistance measurements that ruthenium, like osmium and iridium, has negligible solubility in gold.

Boron

Buddery and Welch[84] have identified the following borides:

Ir_3B_2 – 3.60 weight per cent boron

IrB – 5.31 weight per cent boron

IrB_2 – 10.08 weight per cent boron

OsB – 5.37 weight per cent boron

OsB_2 – 10.22 weight per cent boron; cubic; a = 7.04 A

Os_xB_y – Unknown composition, richer in boron than OsB_2

$Pd_3B_2(?)$ – 6.33 weight per cent boron; hexagonal; a = 6.43 A, c = 3.43 A

Pt_3B_2 or PtB – In the range 3.5 to 5.25 weight per cent (40 to 50 atomic per cent) boron; a tentative structure of PtB was given as tetragonal, a = 2.78 A, c = 2.96 A; between platinum and this phase a "complex region" was observed; additions of boron appear to lower the melting point of platinum considerably[85]

Rh_2B – 4.99 weight per cent boron; orthorhombic; 8 rhodium atoms per unit cell; a = 5.42 A, b = 3.98 A, c = 7.44 A

RhB – 9.51 weight per cent boron

Rh_xB_y – Greater boron content than RhB_2; Mooney and Welch[86] have observed an additional phase between Rh_2B and RhB, although an identification of this phase has not been made

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Ru$_2$B – 5.05 weight per cent boron

RuB – 9.62 weight per cent boron, cubic, a = 6.98 A

Ru$_2$B$_3$ – 13.76 weight per cent boron

RuB$_2$ – 17.55 weight per cent boron.

Reinacher[87] reported that boron forms a low-melting eutectic with all of the platinum-group metals. The melting points of the eutectics are as follows: iridium, 1046 C, osmium >1500 C(?), palladium, 743 C, platinum, 800 C, rhodium, 1131 C, and ruthenium, 1370 C.

Barium

Platinum. Heumann[88] has identified the compound BaPt$_5$ as a hexagonal CaCu$_5$-type structure, six atoms per unit cell, with a = 5.505 A and c = 4.342 A. This phase is stable only at elevated temperatures; however, complete decomposition on cooling can be prevented by quenching.

Beryllium

Compound phases in systems of the refractory platinum metals with beryllium have been studied by Misch[89] and Kaufmann, Gordon, and Lillie.[90] Compounds and their compositions and solubility limits, where available, are summarized below:

Be$_2$Ir – 8.54 weight per cent beryllium

Be$_2$Os – 8.66 weight per cent beryllium; alloy of 20 weight per cent
beryllium as cooled from the melt is two phase with 20 to 30
per cent eutectic

Be$_2$Rh – 14.9 weight per cent beryllium; complex powder pattern similar
to Be$_2$Ir; alloy of 90 weight per cent beryllium as cooled from
the melt is two phase with a eutectic network

Be$_2$Ru – 15.06 weight per cent beryllium; complex powder pattern simi-
lar to alloy of Be$_2$Os (90 weight per cent beryllium) as cooled
from the melt is two phase, with about 20 per cent eutectic
and a fine precipitate in the primary beryllium.

Palladium. Palladium-rich alloys of the palladium-beryllium system have been studied by several investigators.[89,90,91,92] One of the important features of this system is the existence of a low-melting eutectic (930 C) at about 2.1 weight per cent (20 atomic per cent) beryllium.

The existence of the following platinum-bismuth compounds has been reported:

PtBi – 51.71 weight per cent bismuth; NiAs (B8)-type structure[97]

PtBi$_2$ – 68.15 weight per cent bismuth; cubic, pyrite (C2)-type structure; a = 6.69 A[98,99]

PtBi$_3$ – 76.25 weight per cent bismuth.[100]

Rhodium. The rhodium-rich portion of the rhodium-bismuth system has not been investigated; in the composition range 65 to 90 weight per cent bismuth, the following compounds have been detected:[101,102]

RhBi – 67 weight per cent bismuth; NiAs (B8)-type structure; a = 4.08 A, c = 5.66 A

RhBi$_2$ – 80.24 weight per cent bismuth

RhBi$_4$ – 89.04 weight per cent bismuth.

Carbon

Moissan[103,104] reports that all of the platinum-group metals dissolve carbon when molten, the carbon being precipitated as graphite on cooling. Investigations of osmium powder exposed to methane at 1200 and 2000 C disclosed no change in lattice parameters.[105]

Collier, et al.,[106] reports that melting platinum in a graphite crucible reduced the melting point of platinum to 1734 C and resulted in an ingot containing 1.2 weight per cent carbon with a structure of primary graphite in a eutecticlike matrix. Lattice-parameter measurements of this material indicate a solid solubility of 0.25 weight per cent carbon in platinum.

Calcium

Vines[82] reports that calcium has a slight solid solubility in platinum.

Cadmium

Investigations of the cadmium-palladium and cadmium-platinum systems by Hume-Rothery, et al.,[107] disclosed the existence of three modifications of the Hume-Rothery γ-phase, in high-cadmium alloys.

The homogeneity ranges of these phases are tabulated below:

| Cadmium-Palladium	Cadmium-Platinum
γ – 81.4 to 84.4 weight per cent (80.7 to 83.3 atomic per cent) cadmium. $a = 9.96$ A at 83.5 weight per cent (82.5 atomic per cent) cadmium	γ – 72.8 to 76.6 weight per cent (82.5 to 85.5 atomic per cent) cadmium. $a = 9.89$ A at 75.0 weight per cent (83.9 atomic per cent) cadmium
γ_i – 78.2 to 80.9 weight per cent (77 to 80 atomic per cent) cadmium; $a = 9.93$ at 79.1 weight per cent (78 atomic per cent) cadmium	γ_1 – 63.8 to 65.8 weight per cent (75.5 to 77 atomic per cent) cadmium
γ_2 – ~74 weight per cent (73 atomic per cent) cadmium	γ_2 – 59.7 to 61.9 weight per cent (72 to 74 atomic per cent) cadmium

At 600 C there appears to be a solid solubility of about 25 and 17 weight per cent cadmium in palladium and platinum, respectively. Below 600 C the limit of solubility of cadmium in platinum seems to decrease, whereas in palladium the limit of solubility appears unaffected by temperature.[108,109] The phase relationships of low-cadmium alloys have not yet been fully investigated, so that no conclusions on the change of cadmium solubility with temperature can be made.

Cobalt

Köster and Horn[110] have investigated alloys of the four refractory platinum-group metals with cobalt. Constitution diagrams for these systems are presented in Figures 18 through 21. In all systems the liquidus and solidus lines are hypothetical, and are based on observations of the experimental alloys and the known melting points of the various metals. Also, the phase boundaries, where represented by broken lines, are hypothetical. In all the figures the lines θ_α and θ_ϵ denote the Curie temperatures of the α and ϵ phases, respectively.

Iridium. Lattice-parameter and microscopic investigations indicate that the face-centered-cubic modification of cobalt forms a continuous series of solid solutions with iridium. The transformation curves in Figure 18 are based on magnetic and dilatometric measurements and give the start of the $\epsilon' \rightarrow \alpha$ transformations on heating and cooling. The transformation curves cannot be considered as true equilibrium curves.

In constructing the hypothetical liquidus and solidus curves, the minimum at about 29.1 weight per cent (57 atomic per cent) cobalt was included because alloys containing 23.2 and 30.5 weight per cent (49.4 and 58.4 atomic per cent) cobalt were partially molten on annealing at 1400 C.[110]
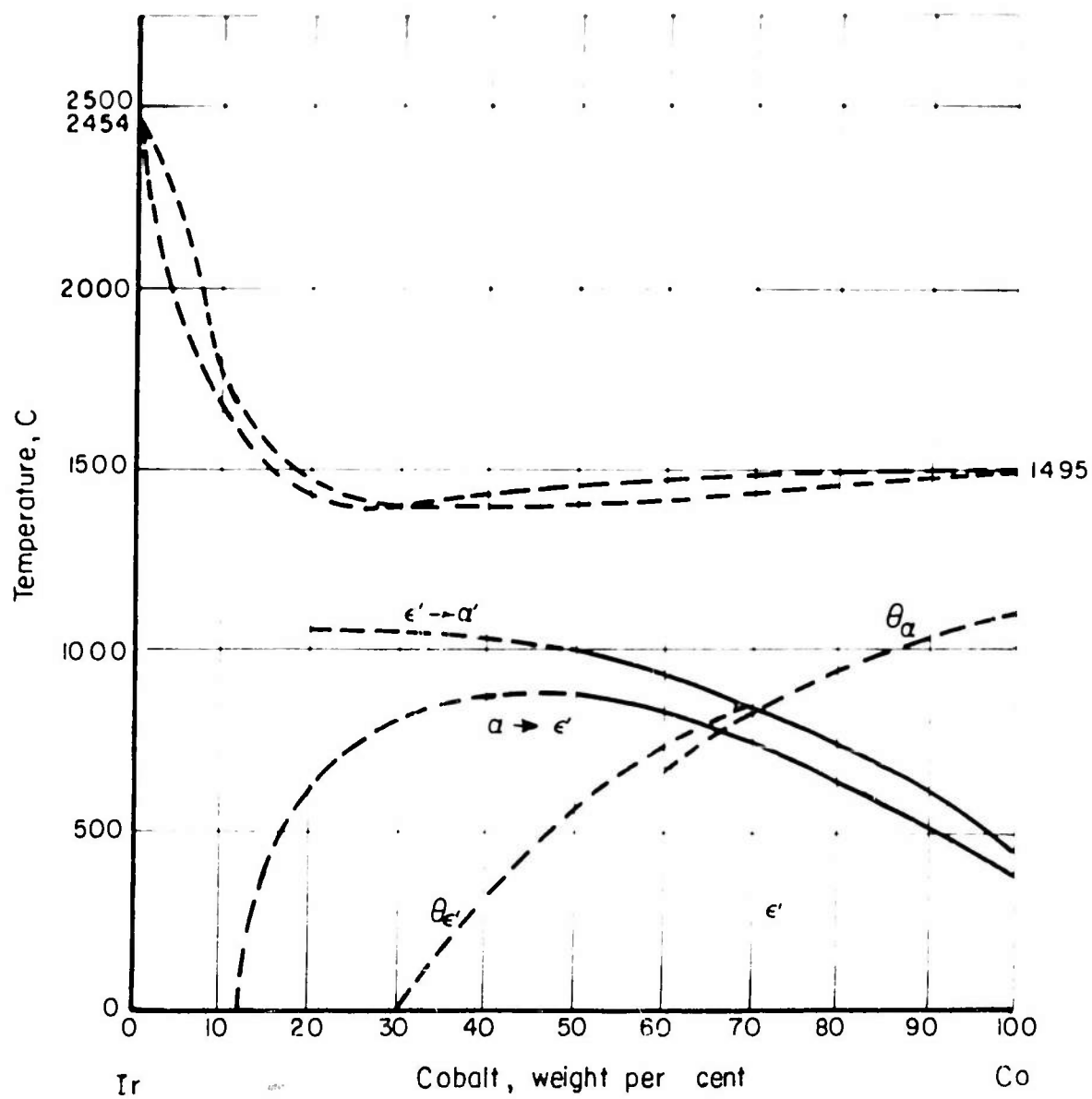
FIGURE 18. CONSTITUTION DIAGRAM OF THE IRIDIUM-COBALT SYSTEM[110]
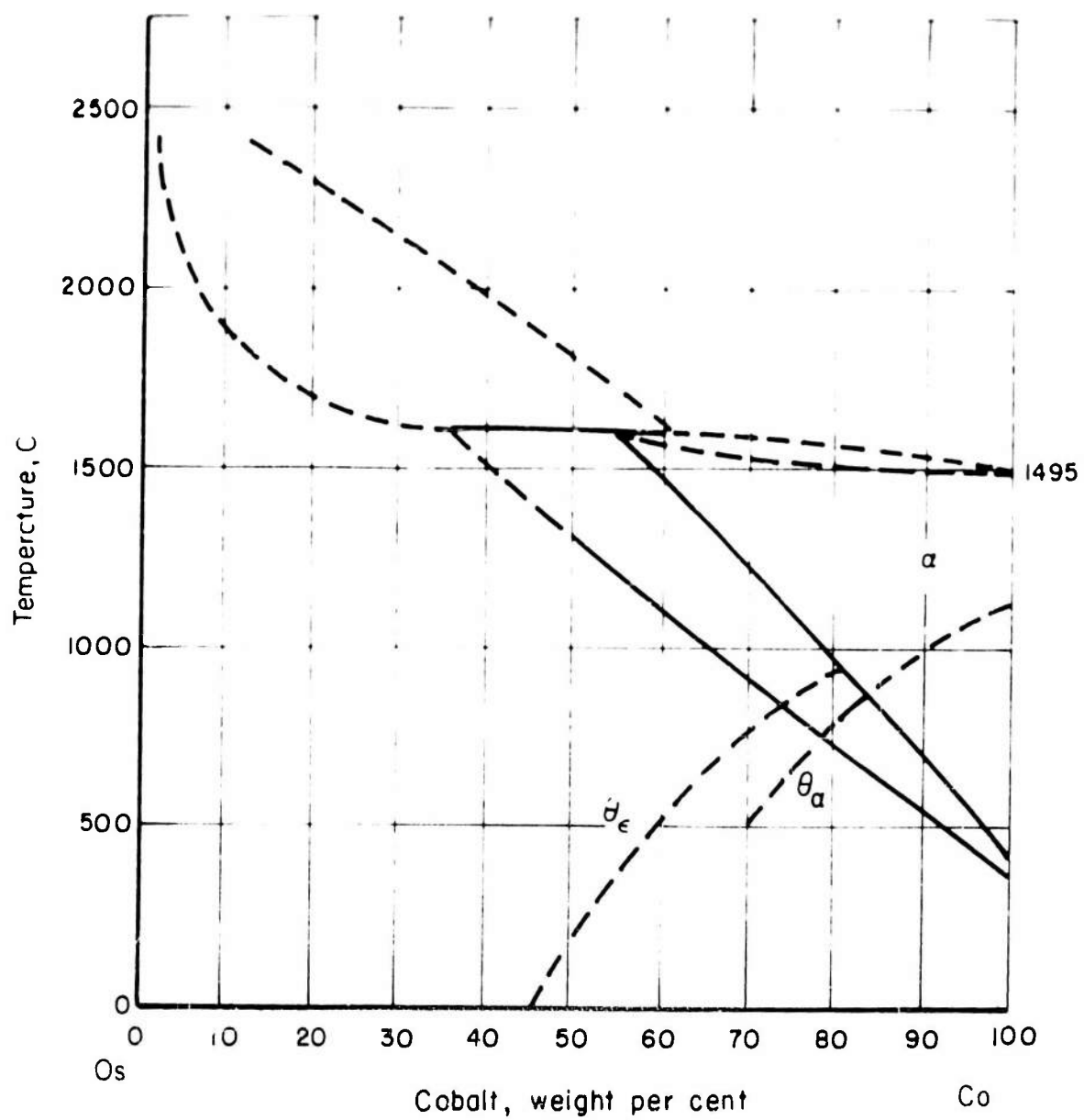
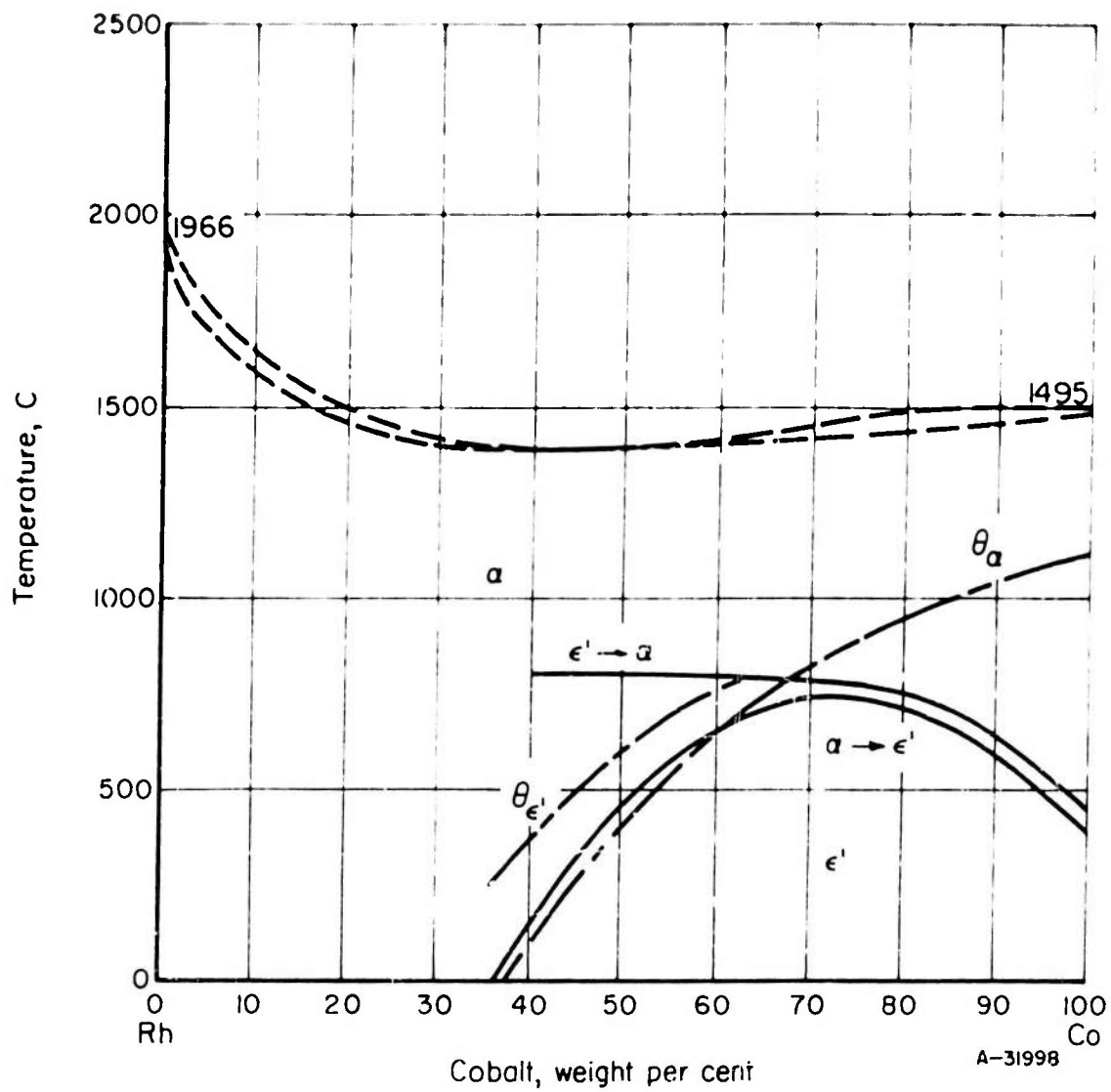FIGURE 19. CONSTITUTION DIAGRAM OF THE OSMIUM-COBALT SYSTEM[110]

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FIGURE 20. CONSTITUTION DIAGRAM OF THE RHODIUM-COBALT SYSTEM[110]
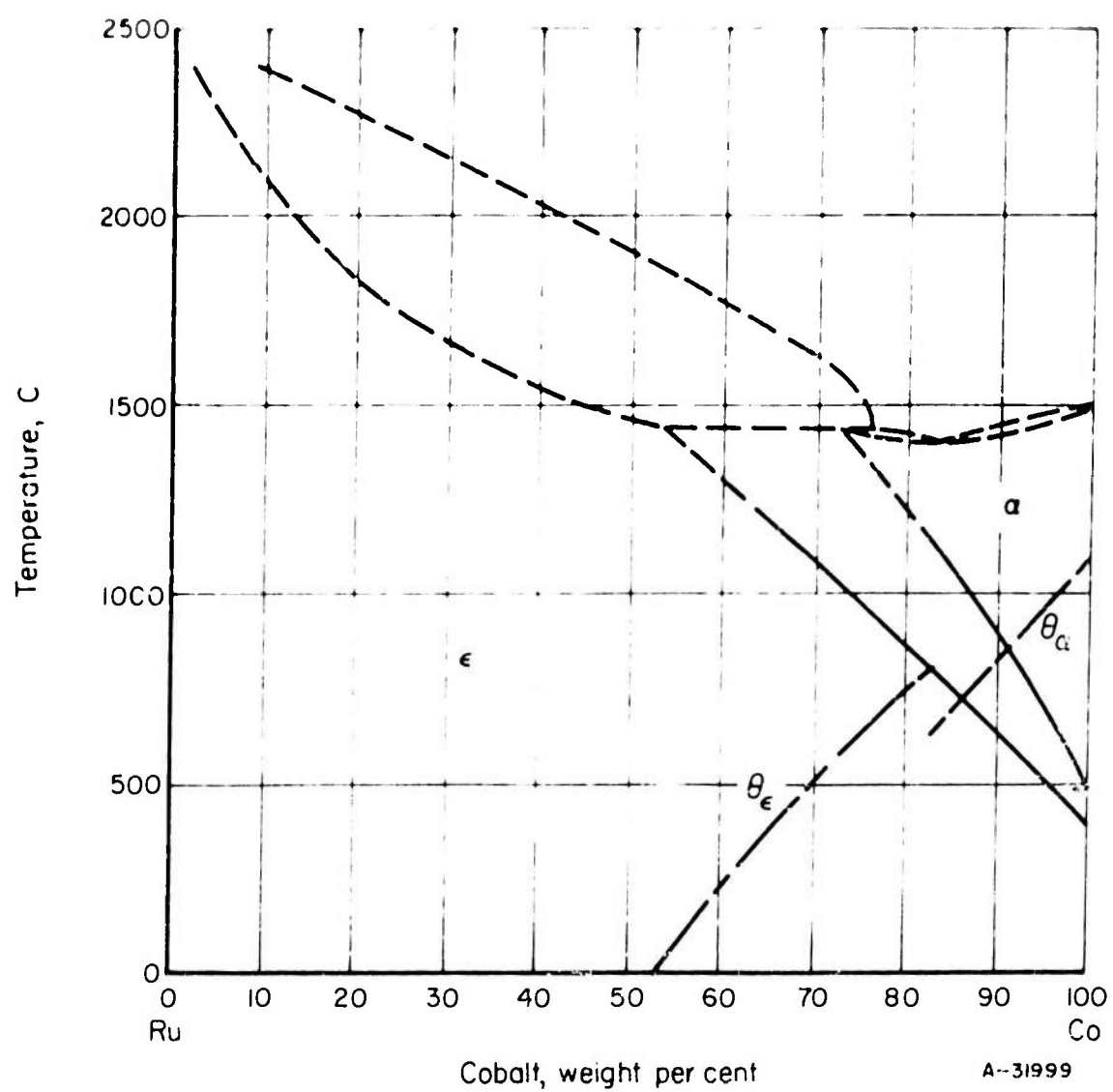
FIGURE 21. CONSTITUTION DIAGRAM OF THE RUTHENIUM-COBALT SYSTEM.(110)

Osmium. In the case of osmium there is a continuous series of solid solutions with the low-temperature hexagonal-close-packed modification of cobalt. The solidification interval of alloys containing 10.5 to 42.1 weight per cent (27 to 70 atomic per cent) cobalt is assumed to be broad because alloys in this range required homogenization anneals about 100 C below the solidus.

Palladium. Palladium forms a continuous series of solid solutions with the high-temperature face-centered-cubic modification of cobalt. Grube and Kästner[111] have established that a minimum in the liquidus curve exists at 1217 C and about 36.9 weight per cent (50 atomic per cent) cobalt. Grube and Winkler[112] using magnetometric measurements have shown the Curie temperature to decrease smoothly from 1119 C for pure cobalt to 0 C at about 4 weight per cent (8 atomic per cent) cobalt. They also have shown that a strong hysteresis occurs for the $\epsilon \rightarrow \alpha$ transformation.

Platinum. Platinum, like the other face-centered-cubic platinum-group metals forms a continuous series of solid solutions with the high-temperature, face-centered-cubic modification of cobalt. Also, like the other metals of the group, a minimum was observed in the liquidus curve at 1430 C and about 48.2 weight per cent (85 atomic per cent) cobalt.[63,113]

Two order-disorder transformations have been observed in the platinum-cobalt system. One has a maximum in the transformation curve at 22.9 weight per cent (50 atomic per cent) cobalt (PtCo) at 825 C.[113,114] The homogeneity range of this face-centered-tetragonal phase [a = 3.793 A and c = 3.675 A at 23 weight per cent (50 atomic per cent) cobalt] extends from 10 to 25 weight per cent (26 to 50 atomic per cent) cobalt. The other order-disorder transformation occurs in the region of 9.0 weight per cent (25 atomic per cent) cobalt (Pt_3Co) with a maximum in the transformation curve lying between 700 and 800 C.[115]

As was observed with palladium-cobalt alloys, the Curie temperature in the platinum-cobalt system decreases smoothly from 1120 C for pure cobalt to 0 C at about 3.5 weight per cent (11 atomic per cent) cobalt.[113]

Rhodium. As with iridium, rhodium forms a continuous series of solid solutions with the high-temperature, face-centered-cubic modification of cobalt. It is interesting to note that the transformation curves, obtained by magnetic and dilatometric measurements, show an increasing transformation hysteresis with decreasing cobalt content. From the phase diagram, Figure 20, it is seen the α to ϵ_1 transformation occurs below room temperature in alloys containing less than 35.4 weight per cent (50 atomic per cent) cobalt. It should be emphasized that the transformation curves presented here are not equilibrium curves but denote the temperatures of the start of the diffusionless $\epsilon' \rightarrow \alpha$ and $\alpha \rightarrow \epsilon'$ transformations on heating and cooling respectively.

Again, as with iridium, alloys containing 15.4 and 29.1 weight per cent (24.8 and 42.8 atomic per cent) cobalt were partially molten on annealing at 1400 C.

Ruthenium. Like osmium, ruthenium forms a continuous series of solid solutions with the low-temperature, hexagonal-close-packed modification of cobalt. The transformation curves presented in Figure 21, represent equilibrium conditions above 1000 C and are nonequilibrium curves below 1000 C.

A minimum in the liquidus curve at about 84.2 weight per cent (90 atomic per cent) cobalt was constructed as alloys containing 81.7 and 85.6 weight per cent (88 and 91 atomic per cent) cobalt were partially molten on annealing at 1400 C.[49]

Chromium

Alloys of chromium with the refractory platinum-group metals have been investigated by Raub[116], Raub and Mahler[117], and Greenfield and Beck[118]. Information on solubility limits and homogeneity ranges of phases are tabulated below:

Metal	Solubility Limit, weight per cent		Homogeneity Range, weight per cent chromium		
	Cr in M	M in Cr	Hexagonal-Close-Packed ϵ-Phase	Cubic β-W Phase	σ-Phase
Iridium	9.7	8.7	11-21.2	41.8-50.0	--
Osmium	22.4 (800-1350 C)	28.1	--	Cr_3Os narrow (a = 4.684 A)	Cr_2Os[a]
Rhodium	4.02 (900 C)	10.6 (800 C)	13.9-43.4 (900 C)	Cr_3Rh	
	14.5 (1200 C)	24.9 (1300 C)	33.8-48.9 (1200 C)	--	--
Ruthenium	21.0 (900 C)	27.2 (900 C)	--	Cr_3Ru (below 950 C)	Cr_2Ru[b]
	25.3 (1300 C)	30.2 (1300 C)	--	--	--

(a) The σ-phase, Cr_2Os, identified by Raub[116], is tetragonal, a = 9.105 A, c/a = 0.516, and stable only at elevated temperatures.

(b) Raub and Mahler also identified a phase, ~Cr_4Ru, formed below 950 C.

In addition to the above phases, in the iridium-chromium system, a ferromagnetic ordered phase of the Cu_3Au type has been observed to form at low temperatures.[117]

Palladium. The palladium-chromium system has been investigated recently.[119] The results of this work show a solid solubility of about 20.8 weight per cent (35 atomic per cent) chromium in palladium at 300 C, rising to about 33.6 weight per cent (51 atomic per cent) chromium at 1313 C, the eutectic temperature. An intermediate phase, CrPd, face-centered tetragonal, a = 3.881 A, c/a = 0.975, has been identified; this phase forms peritectoidally below 570 C.

Platinum. Investigations of the platinum-chromium system[113] have shown that chromium has a high solid solubility, 39.9 weight per cent (71 atomic per cent) up to 1000 C in platinum, and that the system is devoid of compound phases. More recent investigations[119, 118] show a lower chromium-solubility limit, 30.6 weight per cent (62 atomic per cent) up to 1400 C, and the existence of an intermediate β-W-type phase, Cr_3Pt. On both sides of this phase, eutectic transformations occurred.

Copper

Palladium. Several investigators report that palladium-copper alloys form a continuous series of solid solutions, and that at low temperatures two order-disorder transformations occur giving rise to ordered structures based on the compositions $PdCu_3$ and $PdCu$.[120, 121, 122] The homogeneity ranges of the ordered phases are subject to several conflicting reports, but most investigators agree on 37.1 to 56.6 and 62.0 to 82.9 weight per cent (50 to 70 and 75 to 91 atomic per cent) copper with maximum temperatures of about 600 and 500 C, respectively.

Platinum. Like palladium, alloys of platinum with copper form a continuous series of solid solutions at elevated temperatures. At lower temperatures two order-disorder transformations occur, one in the range 2.7 to 44.4 weight per cent (8 to 71 atomic per cent) copper embracing the compound compositions Pt_7Cu, Pt_3Cu, and $PtCu$, and the other in the range 45.6 to 97.3 weight per cent (72 to 99 atomic per cent) copper, including the composition $PtCu_5$.

The maxima in the transformation curves occur at 812 C at 24.6 weight per cent (50 atomic per cent) copper and 645 C at 56.9 weight per cent (80 atomic per cent) copper.[120, 123]

The structures of the ordered phases, $PtCu$, Pt_3Cu, and Pt_7Cu are similar to that of a unit cell containing 32 atoms on a parameter twice as large as that for the disordered structure.[123]

Rhodium. A tentative constitution diagram of the rhodium-copper system is presented in Figure 22. The data reported in this study are limited, hence the constitution diagram is considered tentative. From the diagram there appears to be a solid solubility of 6.3 weight per cent (10 atomic per cent) copper in rhodium and 29.0 weight per cent (20 atomic per cent) rhodium in copper at 800 C.[124]

Iron

There is no information presently available on the systems iron-iridium, -osmium, and -ruthenium for alloys rich in the platinum metals. Work on iron-rich alloys has been done by Wever[125], Fallot[126], and Gibson and Hume-Rothery[127]. This information is not presented because it contributes little to the knowledge of the platinum-rich alloys which are of primary interest here.
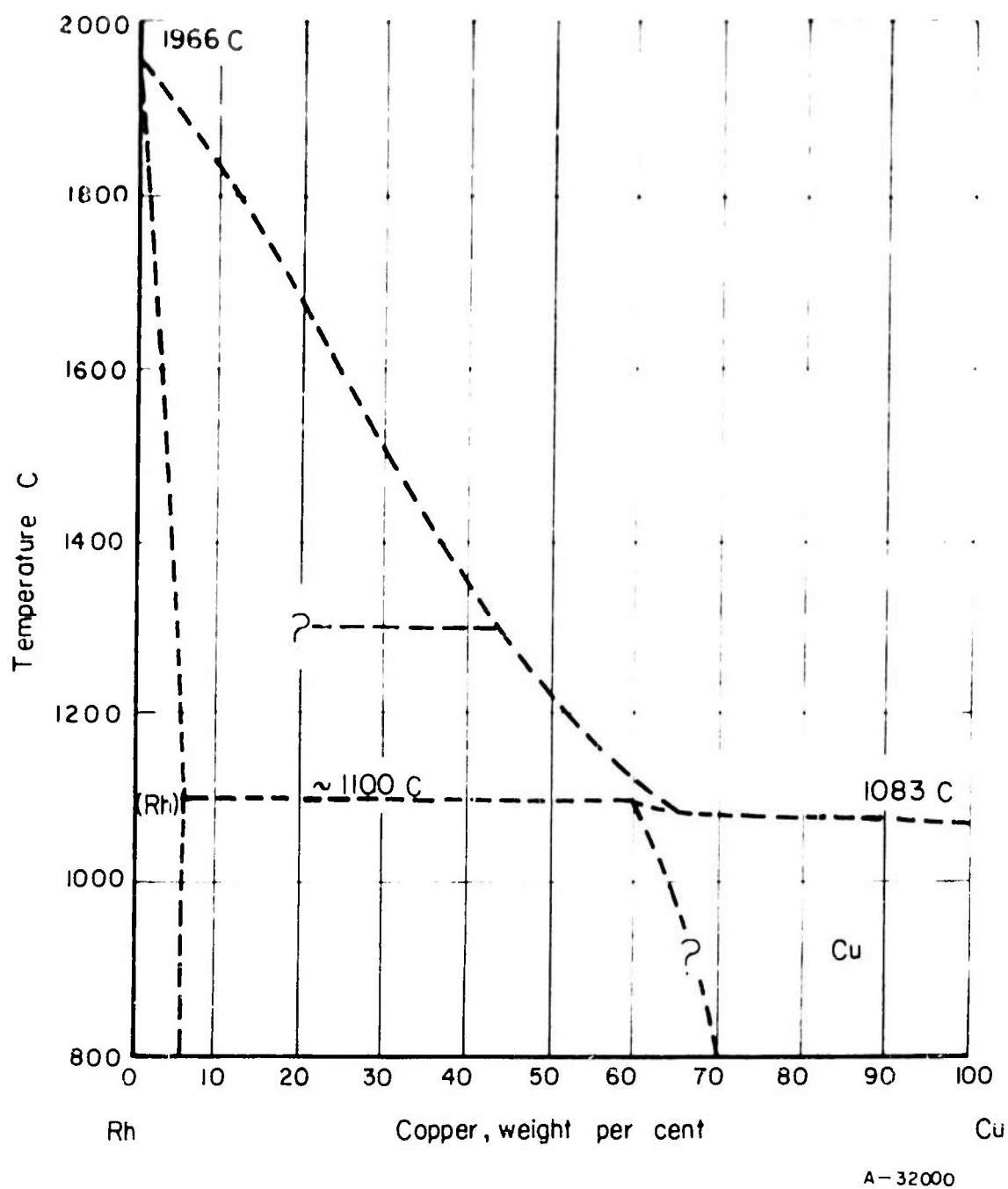
FIGURE 22. TENTATIVE CONSTITUTION DIAGRAM OF THE
RHODIUM-COPPER SYSTEM[124]

Palladium. Grigorjew[128] has established the existence of a minimum in the liquidus curve at about 1310 C and 34.7 weight per cent (50 atomic per cent) iron, and the presence of an ordered phase $FePd_3$ with a maximum on the transformation curve at 16.1 to 17.6 weight per cent (26.2 to 28.5 atomic per cent) iron and 810 C. Otherwise, palladium forms a continuous series of solid solutions with the elevated-temperature γ-modification of iron.

A second order-disorder transformation in the range 24.1 to 44.5 weight per cent (37.4 to 60 atomic per cent) iron has been reported.[129,130] This second-ordered structure, with the theoretical composition FePd, has a maximum at 24.9 to 26.2 weight per cent (38.5 to 40 atomic per cent) iron and 880 C.

The structures of these two ordered phases are: $FePd_5$, isotypic with Cu_3Au (Li_2 type), a = 3.848-3.851 A at 15.2 weight per cent (25 atomic per cent) iron, and FePd, face-centered-tetragonal, a = 3.860 A, c = 3.730 A at 33.1 weight per cent (48.1 atomic per cent) iron.[131]

Platinum. Like palladium, platinum forms a continuous series of solid solutions with γ-iron at elevated temperatures. At lower temperatures, in addition to the $\gamma \rightarrow \alpha$ transformation, three order-disorder transformations have been noted in iron-rich alloys.[126,130,132,133] These transformations in order of increasing iron content are tabulated below:

$\gamma \rightarrow FePt_3$ – 8 to 10.2 weight per cent (23 to 28 atomic per cent) iron;
    maximum between 700 and 800 C; Cu_3Au (Li_2)-type
    structure[133]

$\gamma \rightarrow FePt$ – Vicinity of 22.6 weight per cent (50 atomic per cent)
    platinum; maximum between 1300 and 1400 C; isotypic with
    CuAu; a = 2.719 A, c/a = 1.369[134]; a = 3.87 A,
    c/a = 0.973[133]

$\gamma \rightarrow Fe_3Pt$ – 37.3 to 55.8 weight per cent (67 to 81 atomic per cent) iron;
    maximum about 835 C; Cu_3Au (Ll_2)-type structure.[133]

All of the ordered phases are ferromagnetic. However, the Curie temperature of $FePt_3$ between 2.1 and 6.8 weight per cent (7 and 20 atomic per cent) iron is about 100 C.[133]

Gallium

Investigations by Hellner and Laves[135] of the gallium-palladium and gallium-platinum systems have disclosed the existence of four intermediate phases. These phases are listed below:

Gallium-Palladium	Gallium-Platinum
$GaPd_3$ – 17.89 weight per cent gallium	GaPt – 26.31 weight per cent gallium
$GaPd_2$ – 24.63 weight per cent gallium	Ga_3Pt_2 – 34.88 weight per cent gallium
GaPd – 39.52 weight per cent gallium	Ga_2Pt – 41.66 weight per cent gallium[136]
Ga_7Pd_3 – 60.39 weight per cent gallium	Ga_7Pt_3 – 45.45 weight per cent gallium

Germanium

Iridium. Two intermediate phases in the germanium-iridium system have been identified. These are IrGe, 27.32 weight per cent germanium, MnP (B31)-type structure with a = 6.281 A, b = 5.611 A, and c = 3.490 A[137]; and Ir$_3$Ge$_7$, 46.73 weight per cent germanium, body-centered cubic, with 40 atoms per unit cell and a = 8.753 A.[138]

Osmium. Wallbaum[139] has identified the phase OsGe$_2$ (43.29 weight per cent germanium) with the same crystal structure as RuSi$_2$, which is of an undetermined tetragonal type.

Palladium. Using microscopic techniques, Pfisterer[137] has shown the existence of a primary palladium solid solution and four intermediate phases: Pd$_5$Ge$_2$ [21.39 weight per cent (28.57 atomic per cent) germanium], Pd$_2$Ge (25.39 weight per cent germanium), PdGe (40.49 weight per cent germanium), and Pd$_4$Ge, stable only at elevated temperatures.

Platinum. The following phases in the germanium-platinum system have been identified by microscopic and X-ray studies:[137]

Pt$_2$Ge – 15.68 weight per cent germanium

PtGe – 27.11 weight per cent germanium; isotypic with MnP (B31)-type structure; a = 6.088 A, b = 5.733 A, c = 3.701 A

Pt$_2$Ge$_3$ – 35.81 weight per cent germanium; isotypic with Fe$_2$P (C22)-type structure; a = 6.68 A, c = 3.53 A.[140]

Rhodium. Geller[141], using X-ray diffraction techniques, has studied alloys in the region 19.2 to 60 weight per cent (25 to 66.7 atomic per cent) germanium. The existence of four phases was determined, three of which are tabulated below:

Rh$_2$Ge – 26.08 weight per cent germanium; orthorhombic, 12 atoms per cell; a = 5.44 A, b = 7.57 A, c = 4.00 A

Rh$_5$Ge$_3$ – 29.74 weight per cent germanium; orthorhombic, 16 atoms per cell; a = 5.42 A, b = 10.32 A, c = 3.96 A

RhGe – 41.37 weight per cent germanium; orthorhombic; MnP (B31)-type structure; a = 5.70 A, b = 6.48 A, c = 3.25 A.

Ruthenium. The intermediate phase RuGe$_2$, 51.81 weight per cent germanium, with an unidentified tetragonal structure similar to RuSi$_2$, has been identified.[139]

Hydrogen

Iridium. A survey of the literature on the hydrogen-iridium system has been made by Smith.[144] The studies reviewed generally are in conflict with one another as to whether iridium is a hydrogen occluder, and in no cases are definite solubility data given.

There are no data available on the effect of hydrogen on the mechanical properties or fabricability of Idium.

Osmium. The adsorption of hydrogen at atmospheric pressure by fine osmium black and annealed (sintered) osmium up to 208 C has been reported.[145] The sintered material showed much lower adsorption values.

Palladium. The hydrogen-palladium system has been studied extensively by many investigators; only the most important features of the system will be mentioned here.

Hydrogen in palladium forms two distinct phases, α and β, the limits of which are strongly dependent upon the hydrogen pressure and temperature. The α- and β-phases, both face-centered cubic. coalesce at 295 C, a pressure of 19.87 atmospheres, and 0.25 weight per cent (21 atomic per cent) hydrogen.[146]

The solubility limit of hydrogen in the α-phase is about 0.02 weight per cent (2.4 atomic per cent) in the range of 200 to 300 C.[147]

Perminov, et al.,[148] have shown the effect of pressure on the solubility of molecular hydrogen in the β-phase. Increasing the hydrogen pressure from 1 to 700 atmospheres resulted in an increase in solubility of 0.7 to 0.9 weight per cent (41.2 to 46.7 atomic per cent) hydrogen at 15 C, and 0.55 to 0.78 weight per cent (35.9 to 43.6 atomic per cent) hydrogen at 88 C.

Smith[144] and Dushman[17] give more extensive reviews of the hydrogen-palladium system.

Platinum. Several investigators[149,150,151] agree that the solubility of hydrogen in platinum is small. The solubility increases with increasing temperature from about 0.12×10^{-2} atomic per cent hydrogen at 409 C to 1.64×10^{-2} atomic per cent hydrogen at 1342 C.[149]

Rhodium. The data of several investigators, as summarized by Smith[144], concerning the solubility of hydrogen in rhodium are conflicting. Smith suggests that the conflicting data are indicative of a variable occlusive capacity of rhodium.

Ruthenium. The adsorption of hydrogen at atmospheric pressure by fine ruthenium black up to 186 C has been investigated.[145]

Smith[144] reports on experiments on the polarization capacity of ruthenium cathodes that indicate a considerable cathodic occlusion.

Hafnium

Nevitt and Schwartz[280] have investigated the existence of the Ti_2Ni-type phase in alloys of the platinum-group metals with hafnium. The Ti_2Ni phase was generally found in alloys containing 30 atomic per cent platinum-group metal after quenching from 1200 C. It was found that in some cases a relatively high oxygen level was required for the stability of the phase. Their observations are summarized below.

Iridium. Examination of a 31.5 weight per cent iridium alloy, containing 600 ppm of oxygen, quenched from 1200 C, revealed it was single phase of the Ti_2Ni type, with a = 12.352 ± 0.001 A, and 94 atoms per unit cell.

Palladium. A study of hafnium-palladium alloys containing 13 to 23 weight per cent palladium, revealed that a nominal Hf_3Pd alloy with 800 ppm of oxygen, annealed at 1200 C, was initially a two-phase structure but developed a single-phase Ti_2Ni-type structure after reannealing. This structure had a lattice parameter of 12.3605 ± 0.0003 A and an oxygen content of 6700 ppm.

Platinum. A hafnium-31.5 weight per cent platinum alloy containing 300 ppm of oxygen, annealed at 1200 C, had a Ti_2Ni-type structure with a = 12.451 ± 0.001 A and 94 atoms per unit cell.

Rhodium. Investigation of 20 and 22.2 weight per cent rhodium alloys revealed the existence of a Ti_2Ni-type structure in both alloys. The 20 weight per cent rhodium alloy showed a two-phase hafnium solid solution and Ti_2Ni structure with a parameter of the Ti_2Ni phase of 12.3255 ± 0.0002 A.

Mercury

Palladium. A study of palladium amalgams containing 11.2 to 34.8 weight per cent (19.2 to 50 atomic per cent) palladium disclosed the existence of three distinct phases as listed below:[142]

Pd_2Hg_5 — 17.8 weight per cent (28.57 atomic per cent) palladium; found over the range 17 to 20.2 weight per cent (27.7 to 32.0 atomic per cent) palladium; similar to the γ-brass structure

Pd_2Hg_3 — Similar to $PtZn_2$; found coexisting with above phase in the range 23.2 to 26.2 weight per cent (35.9 to 39.8 atomic per cent) palladium

$PdHg$ — CuAu ($L1_0$)-type structure with a = 4.284 A, c = 3.692 A.

Also, an indication of a fourth phase with about 15.2 weight per cent (25 atomic per cent) palladium was found.

Platinum. Investigations by Bauer, et al.,[143] of the whole composition range disclosed the existence of three intermediate phases. The solid solubility of mercury in platinum was also determined parametrically as 18.1 weight per cent (18.5 atomic per cent) mercury after a 450 C anneal.

The intermediate phases and their structures are as follows:

$PtHg_4$ – 19.57 weight per cent platinum; body-centered-cubic, with 10 atoms per cell; a = 6.18 A

$PtHg_2$ – 32.73 weight per cent platinum; tetragonal, with 3 atoms per cell; a = 4.67 A, c – 2.91 A

PtHg – 49.32 weight per cent platinum; isotypic with CuAu ($L1_0$)-type structure; a = 4.20 A, c = 3.82 A.

Indium

Palladium. Hellner and Laves[135] report the existence of the following phases in the palladium-indium system:

Pd-rich solid solution – about 21.2 weight per cent (20 atomic per cent) indium

Pd_3In – 26.39 weight per cent indium; face-centered tetragonal; a = 4.07 A, c = 3.80 A

Pd_2In – 34.97 weight per cent indium; apparently forms as a result of a solid-state transformation

PdIn – 51.82 weight per cent indium; isotypic with CsCl (B2)-type structure; a = 3.25 A

Pd_2In_3 – 61.73 weight per cent indium; isotypic with Ni_2Al_3 ($D5_{13}$)-type structure; hexagonal, with one formula weight per unit cell; a = 4.53 A, c = 5.50 A

$PdIn_3$ – A phase of approximately 76.34 weight per cent indium, having a "γ-brass structure with voids"; a = 9.44 A.

Platinum. The following intermediate phases have been identified by X-ray analysis:

$PtIn_2$ – 54.05 weight per cent indium. Isotypic with CaF_2 (C1)-type structure, a = 6.366 A(152), stable at elevated temperatures; decomposes to form Pt_2In_3

Pt_2In_3 – 46.86 weight per cent indium; isotypic with Ni_2Al_3 ($D5_{13}$)-type structure, hexagonal, with one formula weight per unit cell. a = 4.53 A, c = 5.51 A(135)

Pt_3In_7 – 57.84 weight per cent indium; isotypic with Ir_3Sn_7, body-centered cubic with 40 atoms per unit cell; a = 9.435 A. (138)

Rhodium Schubert, et al.,(153) reports the compound RhIn to have a CsCl (B2)-type structure, with a = 3.20 A.

Iridium

Osmium. Iridium and osmium occur as a natural alloy, osmiridium, containing between 30 and 65 weight per cent osmium, and platinum, rhodium, and ruthenium in varying amounts.(154)

X-ray investigation of the natural alloy indicates that the iridium-rich solid solution extends to 31 to 35 weight per cent osmium.(155) At higher compositions a hexagonal-close-packed osmium-rich single phase was observed.(156)

Examination of cast iridium-osmium alloys containing 38.7, 59.4, and 79 weight per cent osmium showed a two-phase structure(157), indicating the existence of a miscibility gap between the terminal solid solutions.

Palladium. A constitution diagram of the iridium-palladium system has not yet been determined. Since the metals are of the same crystal structure and their atomic radii differ by less than 1 per cent, they would be expected to form a continuous series of solid solutions.

Platinum. A constitution diagram of the iridium-platinum system, compiled from the data of several investigators(158, 159, 160, 161) is presented in Figure 23.

Alloys of platinum and iridium form a continuous series of solid solutions at elevated temperatures; however, at lower temperatures, a miscibility gap, with a maximum at 50 weight per cent (50 atomic per cent) platinum and 975 C, extends over nearly the whole composition range. This transformation was first observed from increases in tensile strength on annealing wires containing up to 25 weight per cent iridium at 700 to 800 C, and was considered due to an ordering reaction. Work by Raub and Plate(161) has shown that the miscibility gap does occur, but the transformation is extremely sluggish.
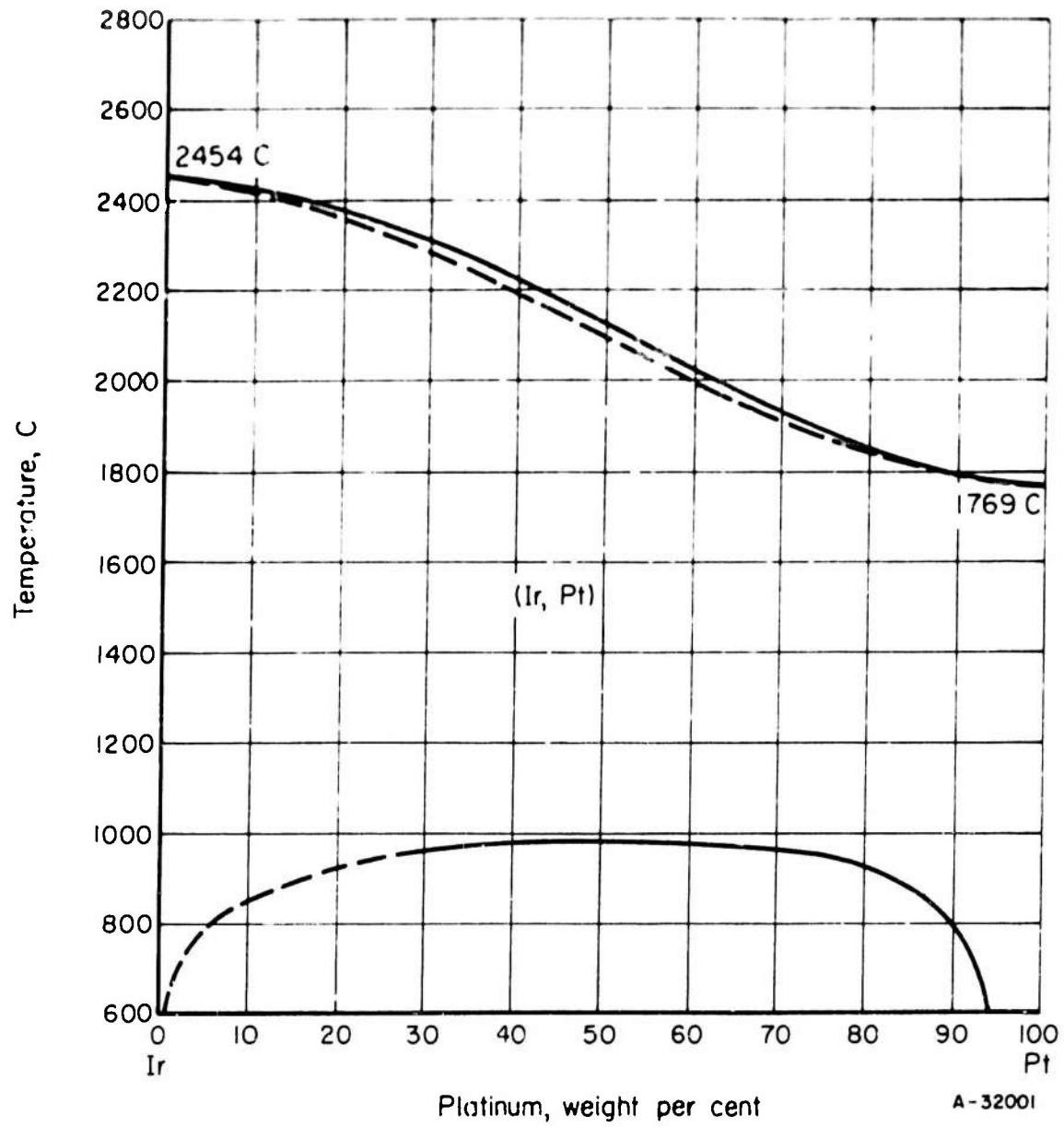
FIGURE 23. CONSTITUTION DIAGRAM OF THE IRIDIUM-PLATINUM SYSTEM [158, 159, 160, 161]

Rhodium. The constitution of the iridium-rhodium system has not yet been investigated. However, both metals are face-centered cubic and their atomic diameters differ by only 0.9 per cent, hence it is probable that they form a continuous series of solid solutions.

Ruthenium. Wartenberg, et al.,[162] reports that the addition of a few per cent ruthenium to iridium raises the melting point of iridium by several hundred degrees C.

Potassium and Lithium

Platinum. It has been reported that platinum is attacked by liquid and gaseous potassium[153], and reacts with molten lithium at a temperature slightly above the melting point, 186 C.[163]

Magnesium

Iridium. Busk[164] found that additions of iridium to magnesium slightly increased the axial ratio of the magnesium.

Osmium. Sauerwald[165] reports that a magnesium-rich eutectic exists.

Palladium. Additions of palladium to magnesium result in a slight increase in the a parameter and a corresponding decrease in the c/a ratio.[164]

Platinum. Hodgkinson, et al.,[166] report that a compound Mg_2Pt (19.94 weight per cent magnesium) is formed by reacting platinum with magnesium vapor in a stream of hydrogen.

Additions of platinum are reported to increase the c/a ratio very slightly.[164]

Rhodium. Additions of rhodium to magnesium decrease the a parameter, resulting in a slight increase in the c/a ratio of magnesium.

Manganese

Iridium. Figure 24 is a partial phase diagram of the iridium-manganese system based on work by Raub and Mahler[118]. The solubility of manganese in iridium is approximately 18.8 and 21.3 weight per cent (44 and 48 atomic per cent) manganese at 650 and 1350 C, respectively. The γ-manganese phase undergoes an order-disorder transformation below 900 C in the region of 46.8 weight per cent (75 atomic per cent) manganese to Mn_3Ir. The ordered structure is of the Cu_3Au type.
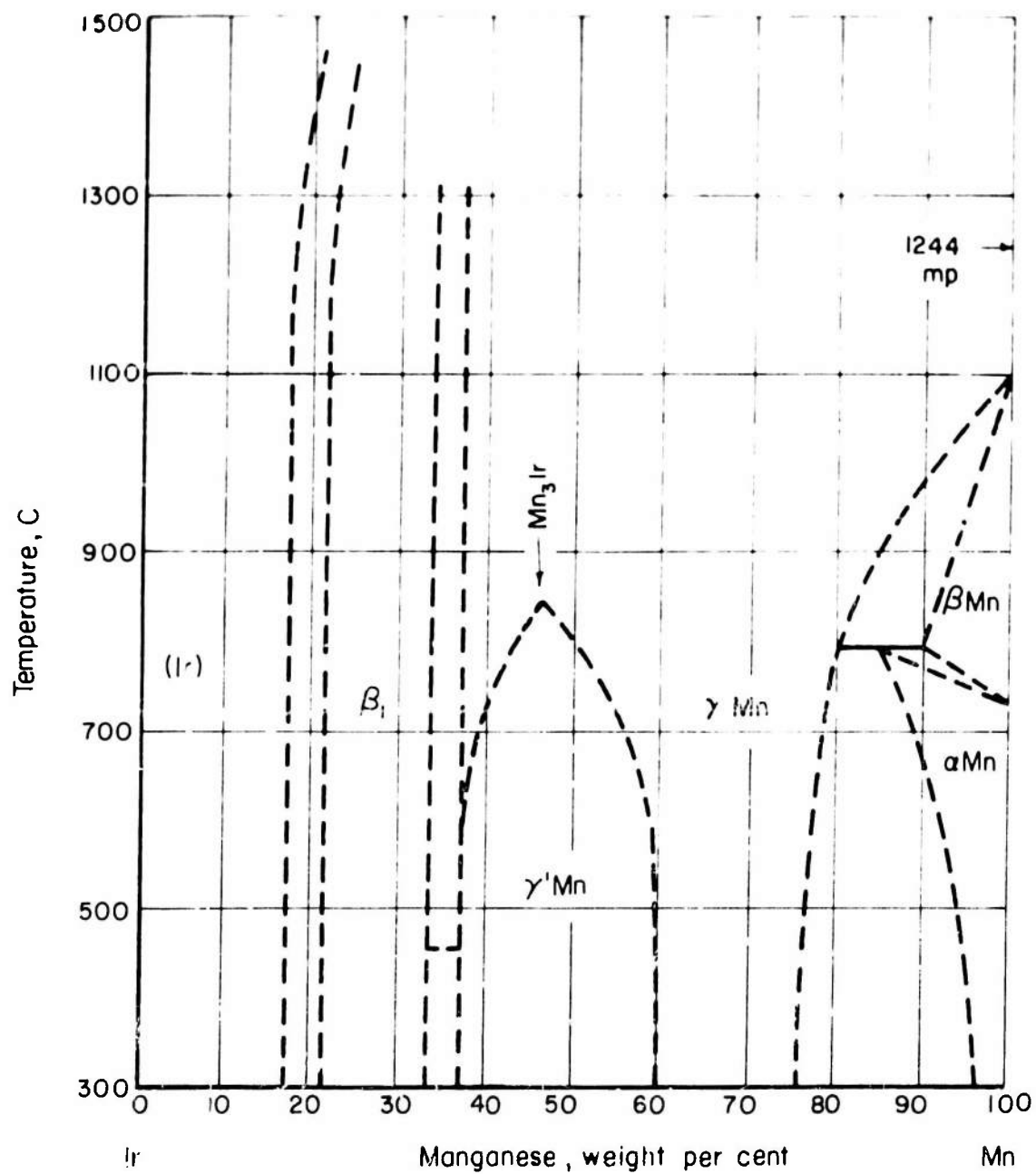
FIGURE 24. PARITAL CONSTITUTION DIAGRAM OF THE IRIDIUM-
MANGANESE SYSTEM[118]

A-32002

Palladium. The entire palladium-manganese system has been studied by several investigators[119, 167, 168], however, only the phase equilibria of palladium-rich alloys will be discussed here.

The limit of solid solubility of manganese in palladium increases from 15.2 weight per cent manganese at 300 C to 18.4 weight per cent at 1350 C, the eutectic temperature.

The solid solubility of palladium in manganese varies from below 10 weight per cent palladium in α- and β-manganese to 30 to 35 weight per cent palladium in γ-manganese.

Platinum. Raub and Mahler[117] report the existence of two order-disorder transformations, γ-manganese → γ´-manganese (Cu₃Au type) below 1050 C in the neighborhood of the composition Mn₃Pt, and platinum-rich solid solution → MnPt₃ (Cu₃Au type) below 1000 C. They also report the solid solubility of manganese in platinum as 14.6 weight per cent manganese up to a eutectic at about 1425 C, and platinum in α- and β-manganese as below 10 weight per cent platinum.

Rhodium. Figure 25 is a partial phase diagram of the rhodium-manganese system based on X-ray and microscopic studies.[117]

The limit of solid solubility of manganese in rhodium is given as about 8.1, 10.7, and 21 weight per cent (14, 18, and 33 atomic per cent) manganese at 800, 1000, and 1300 C, respectively, whereas the limit of rhodium in α- and β-manganese is below 5 weight per cent rhodium.

As in the iridium-manganese system, the γ-manganese phase becomes ordered to a Cu₃Au-type structure, below 900 C, in the neighborhood of the composition Mn₃Rh.

Ruthenium. Raub and Mahler[117] report that no intermediate phase exists in the system ruthenium-manganese. It would seem that the osmium-manganese system might be similar to the ruthenium-manganese system in that the atomic diameters of osmium and ruthenium are about the same. The partial phase diagram, Figure 26, is based on their work.

Molybdenum

Iridium. A study of iridium-molybdenum alloys, between 2.6 to 70 weight per cent (5.2 to 82.4 atomic per cent) molybdenum, by Raub[169] revealed the existence of the following phases:

An iridium-rich solid solution containing up to 8.9 weight per cent (16.2 atomic per cent) molybdenum
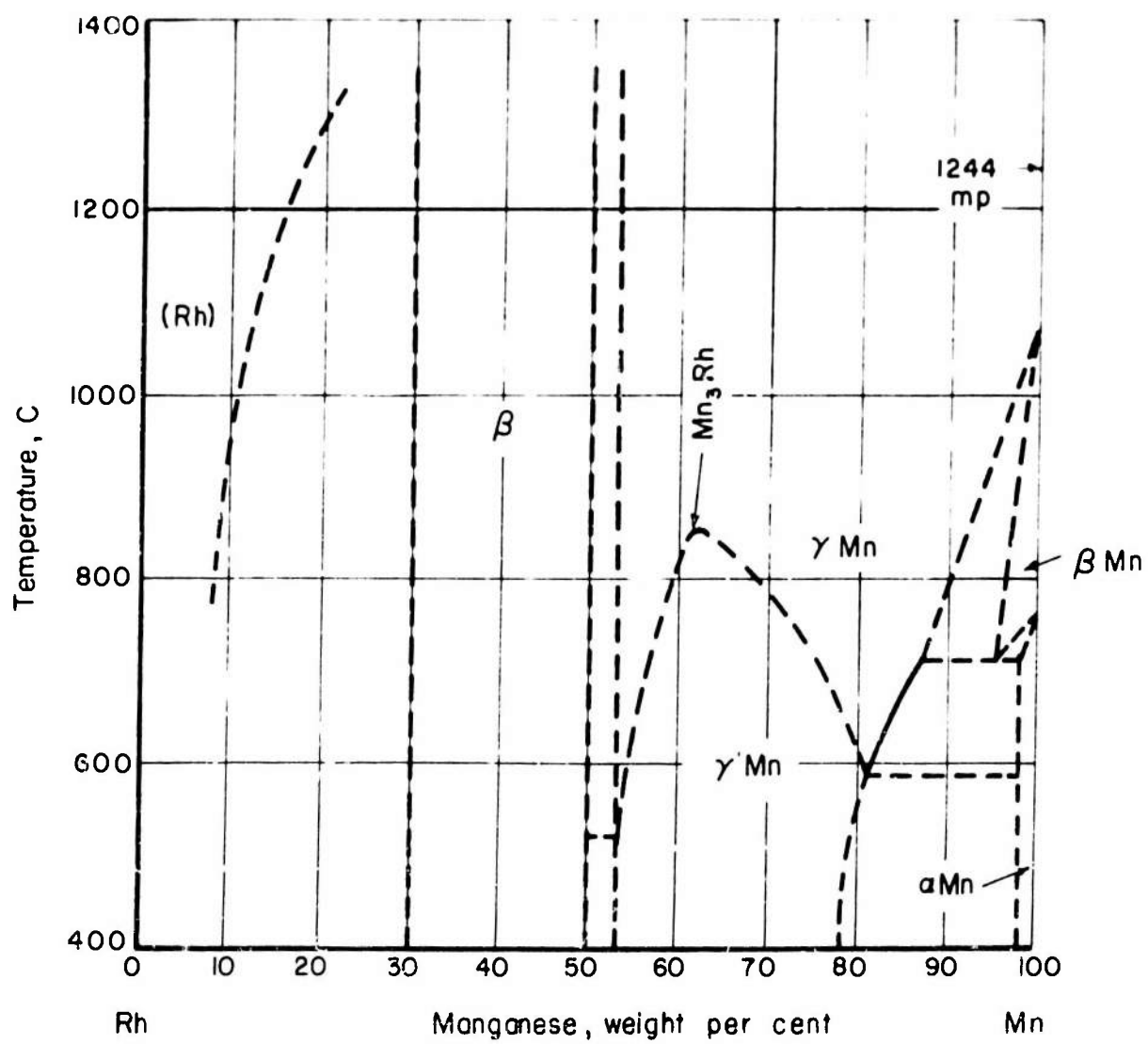
A-32003

FIGURE 25. PARTIAL CONSTITUTION DIAGRAM OF THE RHODIUM-
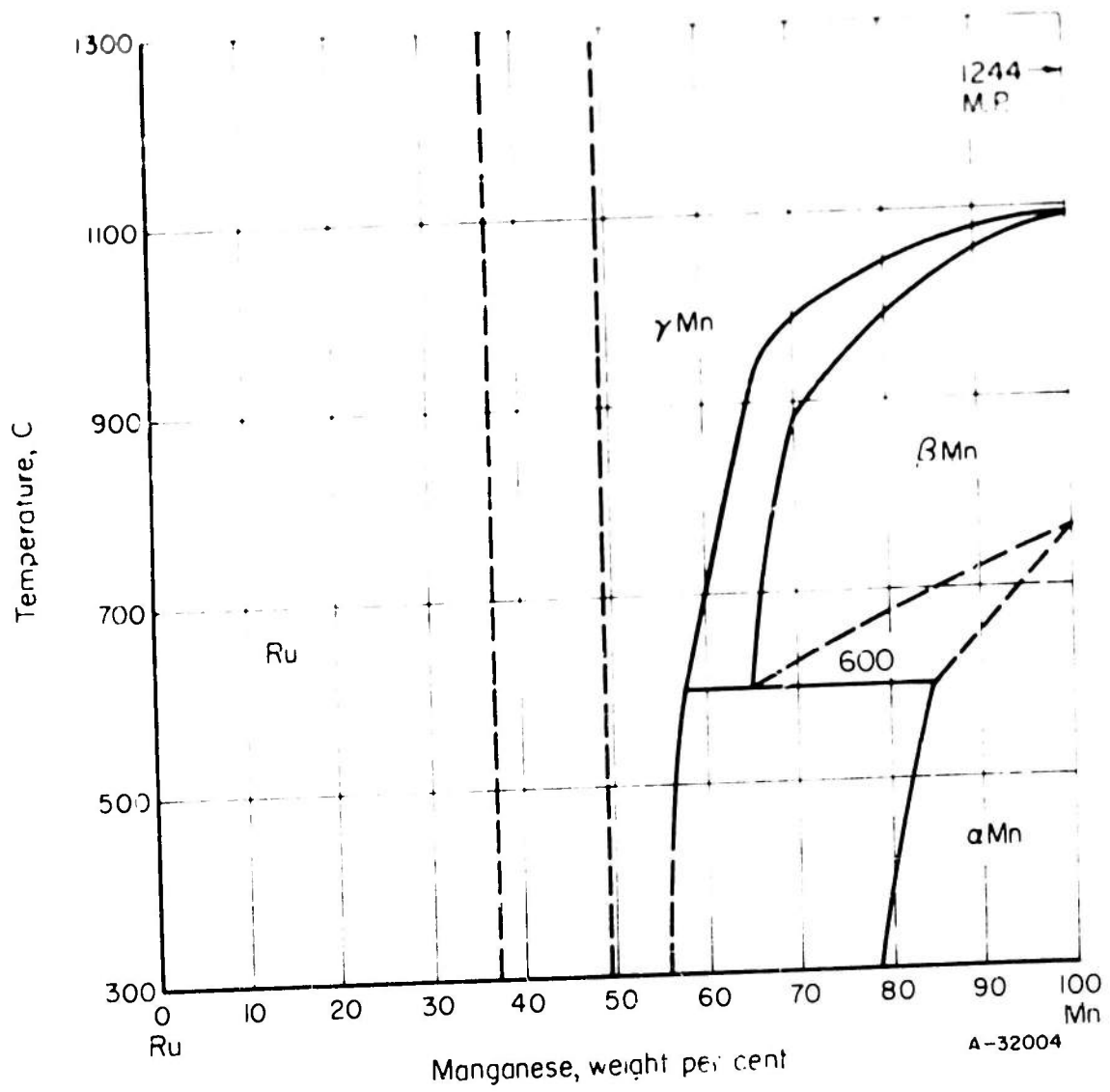MANGANESE SYSTEM(117)

FIGURE 26. PARTIAL CONSTITUTION DIAGRAM OF THE RUTHENIUM-MANGANESE SYSTEM[117]

A hexagonal-close-packed phase, ϵ, between 12.0 and 41.7 weight per cent (21.5 and 59 atomic per cent) molybdenum; a = 2.736 A, c = 4.378 A; and a = 2.771 A, c = 4.436 A at 12 and 40 weight per cent molybdenum, respectively.

Mo_3Ir, 59.85 weight per cent molybdenum, coexisting with almost pure molybdenum, isotypic with β-W (A15-type), a = 4.959 A (mean).

Osmium. A study of three osmium-molybdenum alloys with 30, 50, and 70 weight per cent (45.9, 66.5, and 82.2 atomic per cent) molybdenum[169] disclosed the existence of the following phases:

A solid solution of molybdenum in osmium of 25.2 weight per cent molybdenum at 1200 C

Mo_5Os_3, 45.68 weight per cent molybdenum, presumably with a σ-type structure[118]

Mo_3Os, 60.2 weight per cent molybdenum, β-W (A15)-type structure.

Palladium. Raub[169] reports that no intermediate phase exists in the palladium-molybdenum system. There is a solid solubility of molybdenum in palladium of 33.2, 35.5, and 44.9 weight per cent molybdenum at 800, 850, and 1200 C, respectively. The solid solubility of palladium in molybdenum appears to be quite small.

With regard to the solubility of palladium in molybdenum, Greenfield and Beck[118] report the solubility of palladium in solid molybdenum to be greater than 23 weight per cent (25 atomic per cent) palladium.

Platinum. A study by Raub[169] of platinum alloys containing 2.5 to 70 weight per cent (5 to 82.6 atomic per cent) molybdenum disclosed the existence of three phases.

At temperatures above 1000 C, the solid solubility of molybdenum in platinum is about 26.3 weight per cent (42 atomic per cent) molybdenum. Alloys containing above 14 weight per cent molybdenum undergo a transformation from a face-centered-cubic to a face-centered-tetragonal structure, α', with a = 3.895 ± 0.004 A, c/a = 1.005 to 1.009 independent of molybdenum content.

In the range 29.7 to 55.8 weight per cent molybdenum there exists a hexagonal phase with a = 2.786 A, c/a = 1.611 at the platinum-rich side of the composition range.

It is interesting to note that unlike the iridium-molybdenum system, the platinum-molybdenum system does not appear to have an intermediate β-W-type structure.

Rhodium. Raub[169] found that only one intermediate phase, ϵ, hexagonal close packed, 14.3 to 50.8 weight per cent molybdenum at 1400 C, exists in the rhodium-molybdenum system between 2.5 to 70 weight per cent molybdenum. The lattice

constants of this phase are a = 2.712 A, c/a = 1.603 at the rhodium-rich side, and a = 2.755 A, c/a = 1.605 at the molybdenum-rich side of the region.

The solubility limit of molybdenum in rhodium was also determined as 6.6 weight per cent molybdenum at 1300 C.

Studies of rhodium-molybdenum alloys[118] agree with the above results with the exception that the homogeneity range of the σ-phase is smaller at 1200 C than is reported at 1300 C by Raub.

Ruthenium. Only one intermediate phase, Mo_5Ru_3 (61.13 weight per cent molybdenum), has been found in the ruthenium-molybdenum system in the range 10 to 70 weight per cent molybdenum between 800 to 1600 C.[169] This is presumably identical with a σ-type phase found at 43.5 weight per cent (60 atomic per cent) molybdenum, with lattice constants a = 9.54 A, c = 4.95 A.[118]

Raub also reports that the solid solubility of ruthenium in molybdenum is small at 1200 C but appears to increase at higher temperatures, and that molybdenum in ruthenium is about 33.8 weight per cent molybdenum between 800 and 1600 C.

Jasonis and Cline[170] report that ruthenium and molybdenum form a low-melting eutectic at about 1900 C. The occurrence of this eutectic is especially valuable in that a mixture of ruthenium and molybdenum powder forms an excellent high-temperature brazing alloy.

Nitrogen

Sieverts and Krumbhaar[171] report that nitrogen is insoluble in palladium up to 1400 C.

Sodium

Platinum is attacked by sodium vapor and by molten sodium above 450 C.[172, 173]

Niobium

Iridium. Geller, et al.,[174] report the existence of Nb_3Ir of the β-W (A15)-type with a = 5.131 ± 0.001 A.

Osmium. An intermediate phase Nb_3Os of the β-W (A15)-type structure with a = 5.121 ± 0.002 A has also been identified.[174]

Palladium. An examination of seven alloys ranging in composition from 45 to 65 weight per cent (48 to 68 atomic per cent) niobium disclosed only one intermediate

phase which exists over a narrow range of compositions around 57 weight per cent (60 atomic per cent) niobium.[118] This is a tetragonal σ-type phase with a = 9.89 A and c = 5.11 A.

Platinum. Greenfield and Beck[118], from a study of seven alloys ranging from 26.6 to 59 weight per cent (43 to 75 atomic per cent) niobium annealed at 1000 C, report the existence of two intermediate phases. One, Nb_3Pt, 58.81 weight per cent niobium, is of the β-W (A15)-type with a = 5.11 A. The parameter of Nb_3Pt is reported to be a = 5.153 ± 0.003 A.[174]

The other phase is a tetragonal σ-phase, existing at about 44.5 weight per cent (62.5 atomic per cent) niobium, with a = 9.89 A and c = 5.11 A.

Rhodium. Alloys of rhodium and niobium containing 50.8 to 74.9 weight per cent (52 to 76 atomic per cent) niobium annealed at 1000 C showed the existence of two intermediate phases.[118]

At about 58.1 weight per cent (60 atomic per cent) niobium a tetragonal σ-phase with a = 9.774 A and c = 5.054 A was found to exist over a small range.

A β-W (A15)-type structure, Nb_3Rh (73.03 weight per cent niobium), with a = 5.115 A also was found.[118]

Ruthenium. A study of six ruthenium-niobium alloys containing between 21 and 67 weight per cent (22 and 68 atomic per cent) niobium annealed at 1200 C revealed several intermediate phases, none of which were conclusively identified.[57] One phase existing at 50 and 51 weight per cent (51 and 52 atomic per cent) niobium was assigned a tetragonal lattice with a = 3.00 A and c = 3.38 A.

It was also determined that the solubility limit of niobium in solid ruthenium is less than 21 weight per cent (22 atomic per cent) niobium, and that of ruthenium in niobium is at least 30.5 weight per cent (32 atomic per cent) ruthenium.

Nickel

Osmium. Köster and Horn[175] conclude on the basis of X-ray, microscopic, hardness, and magnetic measurements on 11 osmium-nickel alloys annealed at 1200 C that only two phases, the terminal solid solutions, exist in the osmium-nickel system. The solid solubility of osmium in nickel is about 15 weight per cent osmium, and that of nickel in osmium is about 16 weight per cent nickel.

Palladium. The work of several investigators[176,177,178] shows that nickel and palladium form a continuous series of solid solutions with a minimum in the liquidus curve at 40 weight per cent nickel and 1237 C.[176]

Marian[177] has shown that the Curie temperature of nickel-palladium alloys decreases smoothly from 356 C for pure nickel to 0 C at about 88 weight per cent palladium.

Platinum. Several investigations have shown that platinum and nickel form a continuous series of solid solutions.(177, 179, 180)

Two order-disorder transformations have been observed at relatively low temperatures (99) A transformation to NiPt has been reported(177) with a maximum in the transformation curve at 645 C and 23.4 weight per cent (50 atomic per cent) nickel and a homogeneity range of 20.5 to 31.7 weight per cent (45 to 60 atomic per cent) nickel at 500 C. NiPt has a tetragonal CuAu $(L1_0)$-type structure, with a = 3.823 A and c = 3.589 A at 23.4 weight per cent (50 atomic per cent) nickel.(177)

The other ordering reaction takes place around the composition Ni_3Pt (47.42 weight per cent nickel). The ordered phase, a Cu_3Au-type structure, has been observed in alloys containing 41 to 54.1 weight per cent (69 to 79 atomic per cent) nickel.(180) Oriani and Jones(181) found the disordering temperature of a 48.2 weight per cent (74.93 atomic per cent) nickel alloy is 580 ± 5 C.

Osmium

Palladium. A constitution diagram of the osmium-palladium system has not yet been determined; since the metals are of different crystal structure, a continuous series of solid solutions would not be expected. The fact that the atomic radii of the metals differ by less than 1 per cent would indicate extensive solid solubility of the metals in each other.

Platinum. The osmium-platinum system, like the osmium-iridium system, shows the existence of a miscibility gap between the terminal solid solutions.

The limit of solid solubility, as determined by metallographic techniques, is less than 11 weight per cent platinum in osmium and slightly less than 25 weight per cent osmium in platinum.(188) The existence of a miscibility gap would indicate that there should be aging response in platinum-osmium alloys.

Phosphorus

Reinacher(87) has observed low-melting eutectics in alloys of the platinum metals, except osmium, with phosphorus. The observed eutectic temperatures are as follows: iridium, 1262 C; palladium, 788 C; platinum, 588 C; rhodium, 1254 C; and ruthenium, 1425 C.

Iridium. Two iridium phosphides, IrP (7.41 weight per cent phosphorus) and IrP$_2$ (24.29 weight per cent phosphorus), have been identified by vapor-pressure and X-ray analysis.[189] IrP$_2$ is stable up to about 1230 C. IrP$_2$ appears to form a eutectic with iridium at about 1300 C containing between 3.86 and 5.87 weight per cent phosphorus.

Osmium. X-ray analysis indicates that osmium forms only one phosphide, OsP$_2$ (24.57 weight per cent phosphorus) of undetermined structure.[190]

Palladium. Four intermediate phases have been identified in the palladium-phosphorus system as tabulated below.[191]

β (Pd$_5$P) – 5.49 weight per cent phosphorus

γ (Pd$_3$P) – 8.82 weight per cent phosphorus

Pd$_5$P$_2$ – 10.40 weight per cent phosphorus

PdP$_2$ – _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ .

Jedele[192] reports that the solubility of phosphorus in palladium is only about 0.01 weight per cent phosphorus. In addition, he noted that small additions of phosphorus to palladium resulted in embrittlement due to the formation of a low-melting eutectic at the grain boundaries.

Platinum. Two intermediate phases, Pt$_{20}$P$_7$ (5.26 weight per cent phosphorus) and PtP$_2$ (24.09 weight per cent phosphorus), and a miscibility gap above 683 C extending from 5.3 to 14.7 weight per cent phosphorus have been identified.[193] The melting point of PtP$_2$ is reportedly above 1500 C.

Jedele[192] reports that the solubility of phosphorus in platinum is 0.005 weight per cent phosphorus and, as with palladium, embrittlement of platinum by small amounts of phosphorus is due to the formation of a low-melting eutectic (588 C) at the grain boundaries.

Rhodium. Four intermediate phases, shown in the incomplete phase diagram, Figure 27, have been identified in the rhodium-phosphorus system.[194] These are: Rh$_2$P (~15 weight per cent phosphorus), Rh$_5$P$_4$(?) (19.40 weight per cent phosphorus), RhP$_2$ (37.58 weight per cent phosphorus), and RhP$_3$ (47.45 weight per cent phosphorus).

Ruthenium. Three intermediate phases, Ru$_2$P(?) (13.22 weight per cent phosphorus), RuP (23.35 weight per cent phosphorus), and RuP$_2$ (37.85 weight per cent phosphorus), have been identified. There appears to be no extended homogeneity range for any of the compounds.[195]
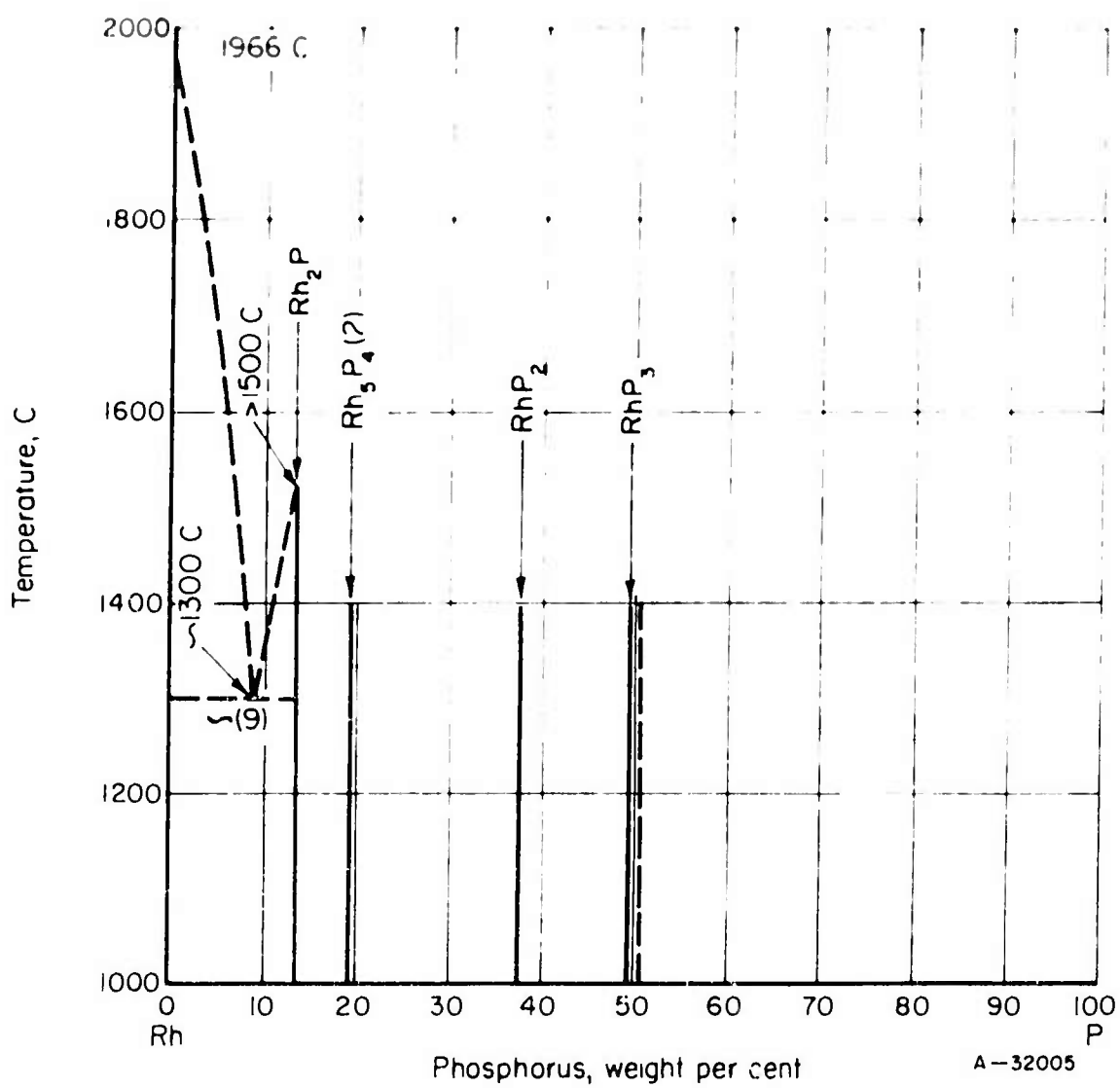
FIGURE 27. PARTIAL CONSTITUTION DIAGRAM OF THE RHODIUM-
PHOSPHORUS SYSTEM(194)

Lead

Iridium. Pfisterer and Schubert[137] report the existence of a peritectically formed intermediate phase, probably IrPb (51.76 weight per cent lead), with the NiAs (B8)-type structure; a = 3.893 A, c = 5.566 A.

Palladium. The following intermediate phases in the palladium-lead system have been identified:

Pd$_3$Pb – 40 weight per cent lead; cubic Cu$_3$Au-type structure, with a = 4.021 A

Pd$_3$Pb$_2$ – 56.42 weight per cent lead; homogeneity range from 54.8 to 56.9 weight per cent (38.5 to 41 atomic per cent) lead; NiAs (B8)-type structure, with a = 4.465 A and c = 5.704 A at the palladium-rich side of the range[196]

PdPb – ~66 weight per cent lead; member of monoclinic translation group, with a = 7.09 A, b = 8.44 A, c = 5.57 A, and β = 71 deg[196]

PdPb$_2$ – ~80 weight per cent lead; tetragonal CuAl$_2$ (C16)-type structure, with a = 6.849 ± 0.005 A and c = 5.833 ± 0.005 A.[99]

The solubility of lead in palladium is about 24 weight per cent lead.[197]

Platinum. Three intermediate phases in the platinum-lead system have been reported and substantiated. These are tabulated below:

Pt$_3$Pb – 26.14 weight per cent lead; cubic Cu$_3$Au (L1$_0$)-type structure, a = 4.053 A[196]

PtPb – 51.49 weight per cent lead; hexagonal NiAs (B8)-type structure, with a = 4.258 A and c = 5.467 A[196]

PtPb$_4$ – 80.94 weight per cent lead; tetragonal unit cell with 10 atoms; a = 6.666 ± 0.001 A and c = 5.978 ± 0.001 A.[198]

Rhodium. Two compounds Rh$_2$Pb[102] (50.17 weight per cent lead) and RhPb$_2$ (80.11 weight per cent lead)[99] have been identified. RhPb$_2$ is of the tetragonal CuAl$_2$ (C16) type with a = 6.664 ± 0.003 A and c = 5.865 ± 0.003 A.

Palladium

Platinum. In spite of the widespread use of platinum-palladium alloys, this system has not yet been thoroughly investigated. Thermal and electrical measurements[199,200] indicate that the two metals form a continuous series of solid solutions at elevated temperatures.

At lower temperatures, between 700 to 1400 C, there is some evidence from hardness measurements of a transformation in the ranges 16 to 54 and 73 to 94 weight per cent (10 to 40 and 60 to 90 atomic per cent) platinum.[201]

Mechanical-property data by Carter[63], and Carter and Stauss[202], show that maxima in hardness and tensile strength occur at about 40 weight per cent palladium.

Rhodium. Tammann and Rocha[201] report that palladium and rhodium form a continuous series of solid solutions with the liquidus curve rising continuously from the melting point of palladium to that of rhodium.

Although no solid-state transformations were indicated, they report that a 15 weight per cent rhodium alloy age hardens slightly, 78 to 110 Bhn, on aging at 550 C. They also report that the maximum hardness is about 145 Bhn at 60 weight per cent rhodium.

Ruthenium. Hellawell and Hume-Rothery[203] have reported lattice parameters of ruthenium-rich solid solutions containing up to 2.74 weight per cent palladium.

No systematic investigation has been made of this system; however, because of different crystal structures, the metals cannot form a continuous series of solid solutions.

Platinum

Rhodium. A constitution diagram of the rhodium-platinum system at elevated temperatures is presented in Figure 28.[158,204]

On the basis of X-ray[204,205], electrical resistivity[204,206], and hardness measurements[204,206], it is concluded that platinum and rhodium form a continuous series of solid solutions.

Platinum-rhodium alloys form one of the most important thermocouple elements for accurate temperature measurement, the platinum-10 and -13 rhodium alloys being used most commonly for this purpose.

The effect of rhodium on the thermal emf of platinum-rhodium versus platinum is well known and will not be presented here. Thermal emf versus composition curves up to 1200 C for the whole range of platinum-rhodium alloys from 0 to 100 per cent rhodium are given by Reference (7).
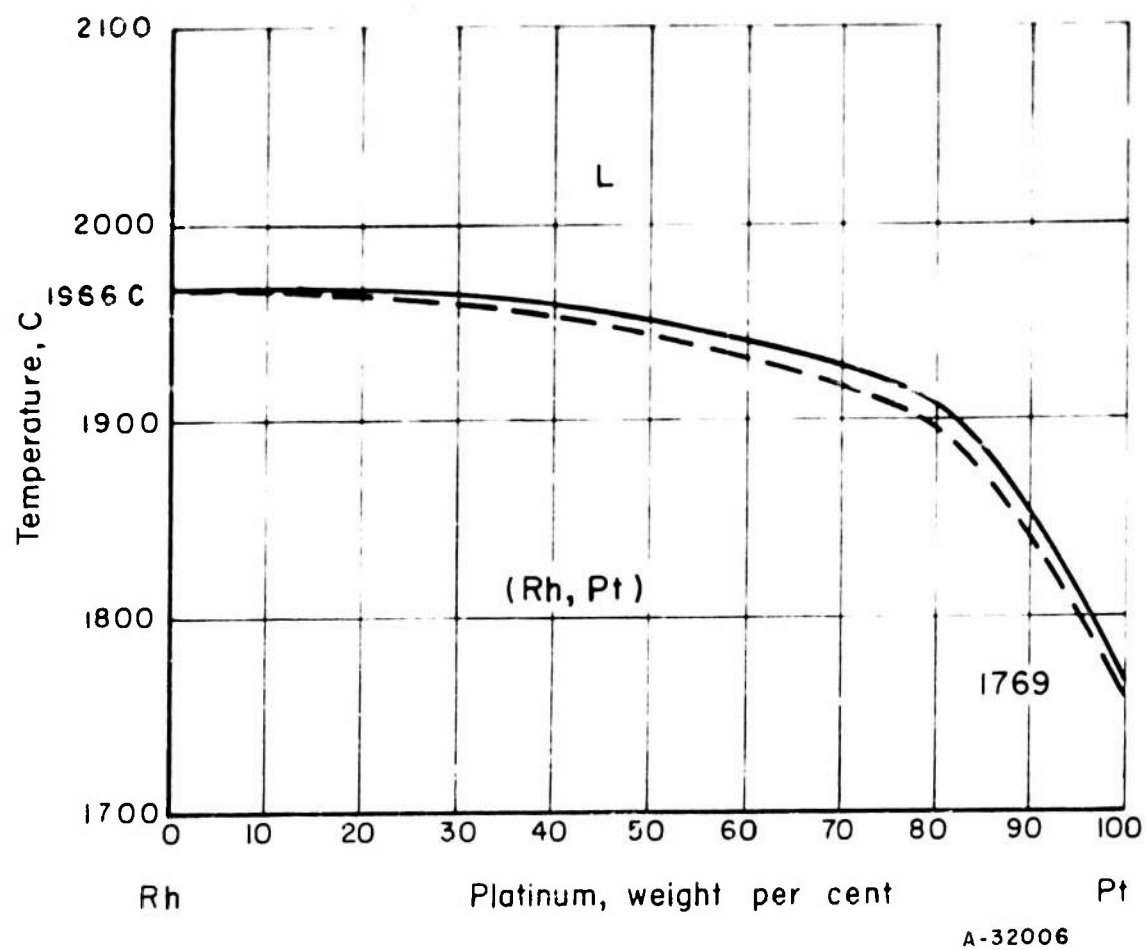
FIGURE 28.   CONSTITUTION DIAGRAM OF THE RHODIUM-
PLATINUM SYSTEM[158, 204]

Ruthenium. Microstructural, electrical-resistance,[207] and X-ray[208] examination indicate that the solubility of ruthenium in platinum exceeds 66.2 weight per cent ruthenium.

Plutonium

Osmium. Konobeevsky[209] reports the solubility of osmium in the three allotropic forms of plutonium to be very slight, less than 0.24 weight per cent osmium. Four intermediate phases have been identified. The compositions of three of these phases correspond to the ideal compositions $PuOs_2$ (28.6 weight per cent plutonium), hexagonal of the $MgZn_2$ (C14) type with a = 5.337 Å and c = 8.682 Å, Pu_5Os_3, and Pu_5Os.

The fourth phase, η, is richest in plutonium and occurs in the range of about 2.4 to 5.6 weight per cent (3 to 7 atomic per cent) osmium.

Rhenium

Iridium. Haas and Schneider[210] report the solid solubility of rhenium in iridium to be at least 5 weight per cent at room temperature.

Osmium. Winkler[188] reports, based on a study of alloys of 25, 50, and 75 weight per cent rhenium, and the similarity of the lattice parameters of the pure metals, that osmium and rhenium form a continuous series of solid solutions.

Palladium. The solid solubility of rhenium in palladium is at least 7.4 weight per cent rhenium.[211]

Platinum. An investigation of the platinum-rhenium system disclosed no intermediate phases, the system being composed of the two terminal solid solutions. The solubility of rhenium in platinum is about 38 to 40 weight per cent rhenium and that of platinum in rhenium 40 to 42 weight per cent platinum up to 2000 C.[212]

Rhodium. Goedecke[213] has reported that alloys containing up to 10 weight per cent rhenium are solid solutions.

Rhodium

Ruthenium. Hellawell and Hume-Rothery[203] have determined the lattice constants of ruthenium-rich solid solutions containing up to 5.3 weight per cent rhodium.

Since the metals are of different crystal structure, it is impossible for them to form a continuous series of solid solutions.

Sulfur

Iridium. The existence of the following iridium sulfides has been shown by X-ray and vapor-pressure measurements between 880 and 1073 C:[214]

Ir_2S_3 - 19.94 weight per cent sulfur

IrS_2 - 24.93 weight per cent sulfur

Ir_3S_8 - 30.69 weight per cent sulfur.

Osmium. Juza[215], on the basis of X-ray and vapor-pressure studies, found that only one sulfide OsS_2 (25.22 weight per cent sulfur) exists. This compound is isotypic with pyrite (C2 type) with a = 5.65 A[216] [a = 5.619 A[217]].

Palladium. Investigations of the palladium-sulfur system have disclosed the existence of the following palladium sulfides:[217,218]

Pd_4S - 6.99 weight per cent sulfur, stable at 25 C

PdS - 23.10 weight per cent sulfur, stable at 25 C

PdS_2 - 37.54 weight per cent sulfur, stable at 25 C

β - between 10 and 11 weight per cent sulfur, stable between 555 and 635 C.

Platinum. Two sulfides, PtS (14.1 weight per cent sulfur) and PtS_2 (24.73 weight per cent sulfur)[219], and a terminal solid solubility of 0.23 weight per cent sulfur in platinum[106] have been reported.

PtS is tetragonal with a = 4.93 A and c = 6.13 A[220], while PtS_2 is isotypic with CdI_2 (C6)-type structure, with a = 3.54 A and c = 5.02 A.[221]

Rhodium. The existence of the following rhodium sulfides has been established: Rh_9S_8, Rh_3S_4, Rh_2S_3, and Rh_2S_5.[222]

Ruthenium. Investigations of the ruthenium-sulfur system indicate that only one ruthenium sulfide, RuS_2 (38.66 weight per cent sulfur) is formed.[223]

Antimony

Palladium. The following tabulation of characteristic temperatures and compositions has been compiled by Hansen from data from two sources[224, 225].

Equilibrium	Reference (224)	Reference (225)
Melting Point of Palladium	1541 C	1549 C
$L \rightleftharpoons (Pd) + \beta$	1070 C, 23.5 weight per cent antimony	1069 C, 23 weight per cent antimony
Melting Point of Pd_3Sb	1220 C	1185 C
$\beta \rightleftharpoons \beta'$ Transformation	950 C	955 C
$L + \beta \rightleftharpoons \gamma$	839 C	850 C
$L \rightleftharpoons \gamma + PdSb$	733 C, 45 weight per cent antimony	731 C, 45.5 weight per cent antimony
Melting Point of PdSb	805 C	800 C
$\gamma \rightleftharpoons \beta + PdSb$	530 C	550 C
$L + PdSb \rightleftharpoons PdSb_2$	677 C	680 C
$L \rightleftharpoons PdSb + Sb$	587 C, 90 weight per cent antimony	593 C, 80.4 weight per cent antimony

The structures of the various phases are as follows:

$\gamma(Pd_5Sb_3)$ – filled NiAs (B8)-type structure; a = 4.45 A, c/a = 1.31 at 660 C[226]

PdSb – isotypic with NiAs (B8) type; a = 4.078 A, c = 5.593 A[227]

$PdSb_2$ – isotypic with pyrite (C2) type, a = 6.452 A.[227]

Platinum. Several investigators agree on the existence of three intermediate phases in the platinum-antimony system. These are:

Pt_4Sb – 13.49 weight per cent antimony[228]

PtSb – 38.41 weight per cent antimony, NiAs (B8) type; a = 4.13 A, c = 5.48 A[229]

$PtSb_2$ – 55.50 weight per cent antimony, isotypic with pyrite (C2 type), a = 6.44 A.[230]

In addition there is a low-melting eutectic at about 24 weight per cent antimony and 633 C[228] or 690 C[231].

Rhodium. Pfisterer and Schubert[101] report the existence of RhSb (54.20 weight per cent antimony), isotypic with MnP (B31) type; a = 6.333 A, b = 5.952 A, and c = 3.876 A.

Selenium

Iridium. The following selenides, prepared by reactions of Se with $IrCl_3$, have been reported: Ir_2Se_3 (38.02 weight per cent selenium); $IrSe_2$ (44.99 weight per cent selenium); an $IrSe_3$ (55.09 weight per cent selenium). [232,233,234]

Osmium. Thomassen[221] reports that the compound $OsSe_2$ (45.36 weight per cent selenium) is isotypic with pyrite (C2 type), with a = 5.945 A.

Palladium. The following palladium selenides have been reported:

Pd_4Se — 15.61 weight per cent selenium

$PdSe$ — 42.53 weight per cent selenium; tetragonal, B34-type structure; a = 6.73 A, c = 6.31 A [153]

$PdSe_2$ — 59.68 weight per cent selenium; orthorhombic, deformed pyrite-type structure; a = 5.72 A, b = 5.80 A, and c = 7.67 A. [153]

Platinum. Two platinum selenides, $PtSe$[98] (28.80 weight per cent selenium) and $PtSe_2$ (44.72 weight per cent selenium),[230] have been reported, although the existence of the former has not been definitely established. $PtSe_2$ is isotypic with CdI_2 (C6 type), with a = 3.73 A and c = 5.07 A. [132]

Rhodium. Biltz, et al.,[234] has prepared Rh_2Se_5 by reaction of the trichloride with selenium, and attempted unsuccessfully to form lower selenides by thermal dissociation of Rh_2Se_5.

Geller and Cetlin[235] report the existence of the phase $RhSe_2$ with a cubic pyrite (C2)-type structure and a homogeneity range from 56.8 to at least 65.8 weight per cent (64-71.4 atomic per cent) selenium.

Ruthenium. Thomassen[230] reports the structure of $RuSe_2$ (60.83 weight per cent selenium) is isotypic with pyrite (C2 type); a = 5.933 A.

Silicon

Iridium. Buddery and Welch[84] report the existence of the following iridium silicides:

Ir_3Si_2 — 8.84 weight per cent silicon

$IrSi$ — 12.70 weight per cent silicon

Ir_2Si_3 – 17.91 weight per cent silicon

$IrSi_3$ – 30.38 weight per cent silicon.

Another silicide, richer in iridium than Ir_3Si_2, was reported but not identified. This silicide is hexagonal with a = 3.96 A and c = 5.13 A. Reinacher[87] reports the existence of an iridium-silicon eutectic, melting at 1470 C.

Osmium. Two silicides, Os_2Si_3 (18.14 weight per cent silicon), tetragonal with a = 5.58 A and c = 5.12 A, and $OsSi_2$ (22.80 weight per cent silicon), have been revealed in an X-ray study of the whole range of compositions.[84]

Palladium. Two palladium silicides, Pd_2Si (11.63 weight per cent silicon) and PdSi (20.84 weight per cent silicon) have been identified. Pd_2Si is isotypic with Fe_2P (C22 type), a = 6.49 A and c = 3.43 A,[84,141] and PdSi is isotypic with MnP (B31 type), a = 6.133 A, b = 5.599 A, and c = 3.381 A.[137]

In addition, three low-melting eutectics have been reported in the palladium-silicon system;[236] the most important from the standpoint of embrittlement of palladium is one at about 4.5 weight per cent (15.5 atomic per cent) silicon and 800 C.

Platinum. Voronow[264] reports the solid solubility of silicon in platinum, after annealing at 800 C, at about 0.2 weight per cent silicon. At the eutectic temperature, 830 C, the solubility should be somewhat higher.

In addition, three platinum silicides have been identified:[264]

Pt_5Si_2 – 5.44 weight per cent silicon

Pt_2Si – 6.71 weight per cent silicon; tetragonal, a = 2.77 A and
   c = 2.95 A[84]

PtSi – 12.58 weight per cent silicon; orthorhombic of the MnP (B31) type; a = 5.93 A, b = 5.59 A, and c = 3.60 A.[137]

Rhodium. Buddery and Welch[84] report the existence of Rh_3Si_2, RhSi, Rh_2Si_3 (or $RhSi_2$), and an unidentified compound lower in silicon than Rh_3Si_2.

Reinacher[87] has observed melting of the eutectic grain-boundary network in a 1.5 weight per cent silicon alloy at 1389 C. He reports the solid solubility of silicon in rhodium to be less than 0.5 weight per cent silicon.

Ruthenium. Reinacher[87] reports that the solid solubility of silicon in ruthenium is less than 0.5 weight per cent silicon. Also, in a 3 weight per cent silicon alloy, melting of a eutectic grain-boundary network is observed at about 1488 C.

Buddery and Welch[84] have identified the following ruthenium silicides by X-ray diffraction techniques:

Ru_3Si_2 – 15.55 weight per cent silicon

$RuSi$ – isotypic with CsCl (B2 type); a = 2.90 A

Ru_2Si_3 – 29.27 weight per cent silicon, tetragonal, a = 5.53 A and c = 4.47 A;[84] this is possibly identical with $RuSi_2$ (35.58 weight per cent silicon), reported to have a tetragonal structure of unknown type.[140]

Tin

Iridium. Nial[237] has identified the phases $IrSn_2$ (55.15 weight per cent tin) and Ir_3Sn_7 (58.92 weight per cent tin) by X-ray analyses. $IrSn_2$ is isotypic with CaF_2 (C1 type), a = 6.338 A, and Ir_3Sn_7 is cubic with 40 atoms per unit cell and a = 9.360 A.

A phase, possibly corresponding to the composition IrSn (38.07 weight per cent tin), isotypic with NiAs (B8 type), a = 3.988 A and c = 5.567 A, has been observed.[196] These investigators also report that tin is soluble in iridium, but the solubility limit is not known.

Osmium. Osmium and tin form no intermediate phase and are reportedly completely insoluble in each other.[237]

Palladium. The following intermediate phases of the palladium-tin system have been positively identified by X-ray analysis:[196]

Pd_2Sn – 35.74 weight per cent tin; orthorhombic, Co_2Si (C37)-type structure; a = 8.12 A, b = 5.65 A, and c = 4.31 A

Pd_3Sn_2 – 42.58 weight per cent tin; partially filled NiAs (B8)-type structure; a = 4.399 A and c = 5.666 A[84] [for 43.8 weight per cent (40 atomic per cent) tin alloy]; homogeneity range 40.2 to 45.5 weight per cent (36 to 41.5 atomic per cent) tin at 480 C[139]

$PdSn$ – 52.90 weight per cent tin; orthorhombic MnP (B31) type; a = 3.87 A, b = 6.13 A, and c = 6.32 A[153]

$PdSn_2$ – 69.01 weight per cent tin; monoclinically deformed B31-type structure; a = 3.93 A, b = 6.18 A, c = 6.38 A, and β = 88.5 deg[238]

$PdSn_4$ – 81.65 weight per cent tin; orthorhombic with 20 atoms per unit cell; a = 6.40 A, b = 6.43 A, and c = 11.44 A.[239]

The solid solubility of tin in palladium was determined[196] as 28 weight per cent tin.

Platinum   Five intermediate phases have been identified by X-ray analysis of platinum-tin alloys.   These are:

Pt$_3$Sn – 16.85 weight per cent tin, isotypic with Cu$_3$Al; a = 4.01 A[240]

PtSn – 37.81 weight per cent tin, NiAs (B8)-type structure, a = 4.111 A and c = 5.439 A[241]

Pt$_2$Sn$_3$ – 47.70 weight per cent tin; hexagonal, of a new type with 10 atoms per unit cell, a = 4.334 A and c = 12.960 A[240]

PtSn$_2$ – 54.87 weight per cent tin, isotypic with CaF$_2$ (C1 type), a = 6.425 A[237]

PtSn$_4$ – 70.86 weight per cent tin; orthorhombic, with 20 atoms per unit cell; a = 6.388 A, b = 6.419 A, and c – 11.357 A.[239]

The solid solubility of tin and platinum has not been determined; however, estimates based on the change in lattice parameter of platinum place it at about 5 weight per cent tin at 750 to 800 C.[237,242]

Rhodium.   The compositions and structures of intermediate phases found in the rhodium-tin system are presented below:

Rh$_2$Sn – 38.58 weight per cent tin; orthorhombic Co$_2$Si-type structure; a = 8.21 A, b = 5.52 A, and c = 4.22 A[153]

Rh$_3$Sn$_2$ – 43.47 weight per cent tin; partially filled NiAs (B8)-type structure; a = 4.340 A and c = 5.553 A at rhodium-rich side of homogeneity range, 41.1 weight per cent (37.6 atomic per cent) tin[196], and a = 4.338 A, c = 5.544 A at the tin-rich side of the homogeneity range, 44.4 weight per cent (40.5 atomic per cent) tin[237]

RhSn – 53.56 weight per cent tin; cubic, of FeSi (B20) type; a = 5.131 A[237]

RhSn$_2$ – 69.76 weight per cent tin; two modifications, with transformation point above 500 C; high-temperature form is tetragonal of CuAl$_2$ type, a = 6.412 A and c = 5.655 A[196]; the low-temperature form is isotypic with CoGe$_2$, orthorhombic unit cell with 7 rhodium and 16 tin atoms; a = b = 6.332 A and c = 11.99 A.[137]

Ruthenium.   Nial[237] has identified a cubic phase in alloys containing 73.6 to 100 weight per cent (70 to 100 atomic per cent) tin annealed at 475 C or quenched from 650 C.   This phase is probably of the composition Ru$_3$Sn$_7$ (73.14 weight per cent tin), with a = 9.351 A and 40 atoms per unit cell.

Tantalum

Osmium. Nevitt and Downey[243] report the existence of a σ-type phase in the approximate composition range 64 to 74 weight per cent (65 to 75 atomic per cent) tantalum at 1200 C. The lattice parameters of a 74 weight (75 atomic) per cent tantalum alloy are: a = 9.934 A and c = 5.189 A.

Palladium. Three arc-melted alloys containing 63.6, 74.0, and 82 weight per cent (50, 62, and 72 atomic per cent) tantalum annealed at 1000 C and quenched showed no evidence of an intermediate phase.[118]

Platinum. Greenfield and Beck[118] report the existence of a σ-phase existing between 66.2 and 69.8 weight per cent (65.8 and 69.5 atomic per cent) tantalum and 81.6 and 83.8 weight per cent (81.5 and 83.5 atomic per cent) tantalum with a = 9.95 A and c = 5.16 A, in alloys quenched from 1000 C.

In alloys containing 57 to 66.1 weight per cent (57 to 65.8 atomic per cent) tantalum, σ was found coexisting with an unidentified intermediate phase.

Rhodium. A study of eight rhodium-tantalum alloys containing 25.9 to 88.5 weight per cent (16.4 to 81 atomic per cent) tantalum quenched from 1000 C revealed the existence of an intermediate tetragonal σ-type phase at about 72.9 weight per cent (60 atomic per cent) tantalum, with a = 9.754 A and c = 5.058 A.[118]

Ruthenium. Microscopic and X-ray investigations of five ruthenium-tantalum alloys containing 40 to 75.1 weight per cent (27 to 62 atomic per cent) tantalum quenched from 1200 C showed the existence of two intermediate phases.[118]

An alloy containing 64.5 weight per cent (50 atomic per cent) tantalum appeared to have a tetragonal structure with a = 3.02 A and c = 3.37 A. Alloys containing about 50.5 and 60.3 weight per cent (36 and 45 atomic per cent) tantalum showed the existence of a second intermediate phase whose structure was not identified.

The solubility limit of tantalum in ruthenium was shown to be less than 40 weight per cent tantalum and that of ruthenium in tantalum at least 26.2 weight per cent (38 atomic per cent) ruthenium.

Tellurium

Iridium. The existence of the compounds $IrTe_2$ (56.9 weight per cent tellurium) and $IrTe_3$ (66.5 weight per cent tellurium) has been reported[234]; however, as yet no systematic investigation of the iridium-tellurium system has been made.

Osmium. The compound $OsTe_2$ (57.30 weight per cent tellurium), isotypic with pyrite (C2 type), a = 6.382 A, has been identified by Thomassen [230]

Palladium. Thomassen [230] reports the existence of two intermediate phases in the palladium-tellurium system. These are PdTe (54.46 weight per cent tellurium), isotypic with NiAs (B8 type) a = 4.135 A, and c = 5.674 A, and $PdTe_2$ (70.52 weight per cent tellurium), CdI_2 (C6)-type structure, a = 4.036 A, and c = 5.128 A

Platinum. The structure of an intermediate phase, $PtTe_2$ (56.66 weight per cent tellurium) was reported [230] as isotypic with CdI_2 (B6), with a = 4.01 A and c = 5.21 A.

Rhodium. X-ray analysis of rhodium-tellurium alloys revealed the existence of the following intermediate phases: [248]

RhTe – Hexagonal NiAs (B8)-type structure; a = 3.99 A

$RhTe_2$ – High-temperature modification (quenched from 1200 C), hexagonal CdI_2 (C6)-type structure; a = 3.92 A and c = 5.41 A

$RhTe_2$ – Low-temperature modification (prepared at 900 C), cubic pyrite (C2)-type structure; a = 6.441 A.

Ruthenium. Thomassen [230] has identified the phase $RuTe_2$ (71.51 weight per cent tellurium) as being isotypic with pyrite (C_2 type), with a = 6.37 A.

Thorium

MgCu2-type Laves phases have been observed in the iridium-thorium and osmium-thorium systems. The phases $ThIr_2$ and $ThOs_2$ were identified as diamond cubic with a = 7.6615 and 7.7050 ± 0.0015 A, respectively. [279]

Titanium

Iridium. Wallbaum [244] investigated the possibility of the occurrence of the phases Ir_2Ti and Ir_3Ti but did not detect these phases.

Osmium. Laves and Wallbaum [244] report the existence of the compound OsTi (20.12 weight per cent titanium) with a CsCl (B2)-type structure, a = 3.07 A. [245]

Palladium. The existence of the following intermediate phases in the palladium-titanium system has been reported:

Pd_3Ti – 13.02 weight per cent titanium, isomorphous with $TiNi_3$
  (DO_{24} type), a = 5.486 A and c = 8.796 A[244]

Pd_3Ti_2 – 23.03 weight per cent titanium[246]

$PdTi_2$ – 47.31 weight per cent titanium, isotypic with Ti_2N. [246]

Platinum. The following intermediate phases have been identified in the
platinum-titanium system:

Pt_3Ti – 7.56 weight per cent titanium; Cu_3Au (L1$_2$)-type structure,
  a = 3.898 A[244]

Pt_3Ti_2 – 14.06 weight per cent titanium[246]

$PtTi_2$ – 32.92 weight per cent titanium, isotypic with Ti_2N[246]

$PtTi_3$ – 42.40 weight per cent titanium; β-W (A15)-type structure;
  a = 5.031 A. [247]

Rhodium. A study of the possible occurrence of the phases Rh_2Ti and Rh_3Ti
indicated these phases do not exist.[244]

Ruthenium. An intermediate phase RuTi (32.02 weight per cent titanium) with a
CsCl (B2)-type structure,[244, 246] a = 3.06 A, has been identified.[245]

Thallium

Palladium. Hellner[249] reports the existence of an alloy of the approximate
composition Pd_2Tl having a structure of the NiAs (B8) type.

Platinum. The existence of an intermediate phase PtTl (51.15 weight per cent
thallium) has been reported[250] and confirmed[251]. PtTl is isotypic with CoSn
(B35 type), a = 5.616 A and c = 4.648 A.[251]

Two eutectics, one at about 98.4 weight per cent thallium and the other at about
40 weight per cent thallium, have been observed.[250] Estimates made on the basis of
lattice-parameter measurements indicated that there was a slight solubility (about
1.5 weight per cent) of thallium in palladium.[251]

Uranium

Iridium. Heal and Williams[252] report the existence of an intermediate phase, Ir$_2$U (38.14 weight per cent uranium) with a face-centered-cubic MgCu$_2$ (C15)-type structure, a = 7.4939 ± 0.0005 kX at 20 C.

Osmium. The compound Os$_2$U (38.5 weight per cent uranium) has been identified as being of the face-centered-cubic MgCu$_2$ (C15) type with a = 7.4974 ± 0.0005 kX at 24 C.[252]

Palladium. Catterall, et al.,[253] studied the palladium-uranium system by means of thermal, metallographic, and X-ray analysis. At the palladium-rich side, a minimum was observed in the liquidus curve at about 28 weight per cent uranium and 1305 ± 5 C. The palladium-rich solid solution reportedly extends to about 38.6 weight per cent uranium; however, Hansen proposes that the minimum in the liquidus corresponds to a eutectic point separating the palladium-rich solid solution from a face-centered-cubic intermediate phase at about 36.1 weight per cent (20 atomic per cent) uranium.

A compound, UPd$_3$ (42.66 weight per cent uranium) has been identified as being of the hexagonal TiNi$_3$ (DO$_{24}$)-type structure with a = 5.769 ± 0.001 A, and c = 9.640 ± 0.001 A at 42.8 weight per cent (24.95 atomic per cent) uranium.[252]

The existence of two other intermediate phases, U$_5$Pd$_6$ and UPd, has been reported.[253]

Platinum. The intermediate phase, UPt$_3$, is reported to be of the hexagonal Mg$_3$Cd (DO19)-type structure, with a = 5.764 ± 0.001 A and c = 4.899 ± 0.001 A.[252]

Saller and Rough[254] report that retention of the β-uranium phase in quenched, low-platinum alloys has been observed. They also report the existence of the compound UPt$_2$ of the hexagonal MgNi$_2$ (C36)-type structure.

Ruthenium. Heal and Williams[252] report the structure of URu$_3$ (43.23 weight per cent ruthenium) is of the cubic Cu$_3$Au (L1$_2$) type with a = 3.988 ± 0.002 A.

Vanadium

Palladium. Greenfield and Beck[118] report that the solubility of vanadium in palladium is approximately 32.5 weight per cent (50 atomic per cent) and that of palladium in vanadium is less than 34.3 weight per cent (20 atomic per cent) palladium.

They also report inconclusive data suggesting the existence of an intermediate phase of unknown structure.

Platinum. An investigation of four platinum-vanadium alloys containing between 14.9 and 44.1 weight per cent (40 and 75 atomic per cent) vanadium, annealed and quenched from 1200 C, revealed the existence of an intermediate phase PtV_3 (43.91 weight per cent vanadium) with a structure of the β-W (A15) type, a = 4.808 A.

The study also showed that the solid solubility of vanadium in platinum is greater than 14.9 weight per cent (40 atomic per cent) vanadium.[118]

Rhodium. Two intermediate phases were found in a study of rhodium-vanadium alloys containing 24.6 to 60.0 weight per cent (40 to 75 atomic per cent) vanadium quenched from 1200 C.

One of these, RhV_3 (59.76 weight per cent vanadium), is of the cubic β-W (A15)-type structure with a = 4.767 A. The other phase was found in an alloy containing 24.6 weight per cent (40 atomic per cent) vanadium and was determined to have a hexagonal-close-packed crystal structure.[118]

Ruthenium. Greenfield and Beck[118] report the existence of an intermediate phase at 34.0 weight per cent (50 atomic per cent) vanadium having a tetragonal lattice with a = 2.96 A and c = 3.09 A.

The solubility limit of vanadium in ruthenium is reportedly less than 10 weight per cent vanadium.

It was also observed that a 47.9 weight per cent (64 atomic per cent) vanadium alloy was single phase with the CsCl (B2)-type structure and cell dimensions similar to those of the vanadium-base solid solutions.[118]

Tungsten

Iridium. Raub and Walter[255] have investigated homogenized alloys containing 5 to 95 weight per cent tungsten. One intermediate phase, β, extending from 22.5 to 55.2 weight per cent tungsten after annealing at 1400 to 1800 C was identified. The lattice constants of this hexagonal-close-packed phase are: a = 2.736 A and c/a = 1.602 at the iridium side, and a = 2.764 A and c/a = 1.611 at the tungsten side of the homogeneity range.

The solid solubility of tungsten in iridium was determined as 19, 13.3, 12.4, and 11.3 weight per cent tungsten at 1800, 1300, 1100, and 900 C, respectively.

Osmium. A study of eight cast alloys containing 15 to 90 weight per cent tungsten revealed the existence of an intermediate phase, probably of the composition W_3Os (74.37 weight per cent tungsten) and terminal solid solutions extending to 47.2 weight per cent tungsten and about 5 weight per cent (5 atomic per cent) osmium.[255]

Studies by Raub[256] suggest that W_3Os may be a σ-phase with a = 9.933 ± 0.007 A and c/a = 0.515.

Palladium. Investigations of the palladium-tungsten system[118,255] revealed no intermediate phases and showed that the solubility limit of tungsten in palladium is close to 30 weight per cent tungsten; palladium is essentially insoluble in tungsten.[255]

The solidus point of a 21 weight per cent tungsten alloy was observed to be slightly below 1400 C.

Platinum. A study of sintered platinum-tungsten alloys by Jaffee and Nielson[257] showed the maximum solubility of tungsten in platinum to be about 62 weight per cent, and that of platinum in tungsten between 4 and 6 weight per cent platinum at the solidus temperature.

Nemilov and Rudnitsky[94] suggest the existence of an ordered phase WPt_3 above 24.5 weight per cent (25 atomic per cent) tungsten, based on hardness and microscopic data.

Rhodium. A study of rhodium-tungsten alloys containing 5 to 80 weight per cent tungsten revealed the existence of the following phases:

A terminal solid solution of tungsten in rhodium up to 20 weight per cent tungsten.

A hexagonal-close-packed phase with a homogeneity range of about 30.3 to 60.4 weight per cent tungsten.

A terminal solid solution of rhodium in tungsten up to about 7.8 weight per cent rhodium.

Greenfield and Beck[118] report the lattice parameters of the hexagonal phase are a = 2.708 A and c = 4.328 A at 30 weight per cent (19.2 atomic per cent) tungsten.

Ruthenium. No intermediate phase was observed in a study of six ruthenium-tungsten alloys containing 10 to 70 weight per cent tungsten.[255] The solubility of tungsten in ruthenium after annealing at 1400 C was found to be about 51.2 weight per cent tungsten.

Obrowski[258] reports the existence of a σ-type phase of the approximate composition W_3Ru_2 (73 weight per cent tungsten), which decomposes eutectoidally into ruthenium and tungsten below 1650 C. The lattice parameters are a = 9.55 A and c/a = 0.52.

Zinc

Osmium. Debray[259] reports that osmium and zinc do not form a compound, based on the fact that osmium-zinc alloys treated with dilute HCl had a residue of pure osmium.

Palladium. The palladium-zinc system is characterized by the existence of several intermediate phases, one of which is a γ-brass-type phase including the ideal composition Pd_5Zn_{21} (72.02 weight per cent zinc).[260]

The solid solubility of zinc in palladium is about 5.5 weight per cent zinc at 530 C and about 12 weight per cent zinc at 780 C.[261]

Platinum. The solubility of zinc in platinum has been found to be greater than about 7 and less than about 10 weight per cent zinc. The existence of several intermediate phases has been reported. These are tabulated below:

ν — Face-centered tetragonal of the CuAl ($L1_0$) type, axial ratio decreases from about 0.954 at the platinum-rich side to 0.860 on the zinc-rich side[109]

ξ — $PtZn_2$, similar to AlB_2 (C32) type with a = 4.11 A and c = 2.744 A at 38.8 weight per cent (64.7 atomic per cent) zinc[109]

$ξ_1$ — Similar to ξ but of lower symmetry[109]

γ — γ-brass-type structure[260]

$γ_1$ — Designated as Pt_5Zn_{21} 59.0 weight per cent (80.77 atomic per cent) zinc a = 18.116 A[109,260]

$PtZn_8$ — 73.8 weight per cent (88.89 atomic per cent) zinc, phase richest in zinc; complicated diffraction pattern indicating low symmetry.[109]

In addition, evidence of an ordered phase Pt_3Zn isotypic with Cu_3Au ($L1_2$) type, a = 3.89 A, and forming at about 800 C, has been found.[109]

Rhodium. Ekman[260] reports the existence of a phase, probably of the ideal composition Rh_5Zn_{21} (72.74 weight per cent zinc), of the γ-brass-type structure.

Zirconium

Iridium. The existence of an intermediate phase $ZrIr_2$ (19.11 weight per cent zirconium) which is isotypic with $MgZn_2$ (C14) type has been reported.[262]

Nevitt and Schwartz[280] report the existence of a Ti_2Ni-type phase in the region 34.5 to 44 weight per cent iridium. The stability of this phase appears to be affected by oxygen content; high oxygen levels promoting stability.

Osmium. Wallbaum[262] reports the existence of the intermediate phase $ZrOs_2$ (19.34 weight per cent zirconium) which is isotypic with $MgZn_2$ (C14) type, with a = 5.189 A and c = 8.526 A.

Palladium. Nevitt and Schwartz[280], in an investigation of the occurrence of a Ti_2Ni-type structure in palladium-zirconium alloys, report this phase does not exist in alloys containing 23 to 44 weight per cent palladium annealed at 700 to 1100 C. A phase was found at 40.5 weight per cent palladium that was tentatively indexed as body-centered tetragonal with a = 3.28 A and c = 3.32 A.[280]

Platinum. The intermediate phase $ZrPt_3$ (13.48 weight per cent zirconium), isotypic with TiN_3 (DO_{24}) type, with a = 5.644 A and c = 9.225 A, has been identified.[244]

A study of platinum-zirconium alloys containing 28 to 47.5 weight per cent platinum annealed at 600 C revealed the existence of an unidentified phase at 38.5 weight per cent platinum and 240 ppm of oxygen. X-ray needles of 34.5 and 41.5 weight per cent platinum alloys containing 6000 ppm of oxygen exhibited a Ti_2Ni-type structure with a lattice parameter of 12.574 ± 0.006 A in 41.5 weight per cent platinum alloy.

Rhodium. Nevitt and Schwartz report the existence of an unidentified phase in equilibrium with the zirconium solid solution in a 32.5 weight per cent rhodium alloy after annealing at 950 C.

Upon reannealing X-ray needles of alloys containing 22 and 24 weight per cent rhodium exhibited a Ti_2Ni-type structure with a lattice parameter of 12.476 ± 0.001 A for the 22 weight per cent rhodium alloy.

The oxygen content of the X-ray needle was 6400 ppm and the oxygen content of the massive 32.5 weight per cent rhodium alloy was 427 ppm, indicating that oxygen may stabilize the Ti_2Ni-type phase in zirconium-rhodium alloys.

Ruthenium. Hellawell and Hume-Rothery[203] report the solubility of zirconium in ruthenium, in alloys strain annealed at 1050 C, at between 0.31 and 0.45 weight per cent zirconium.

The existence of the intermediate phase $ZrRu_2$ (30.96 weight per cent zirconium), isotypic with $MgZn_2$ (C14) type with a = 5.141 A and c = 8.507 A has been reported by Wallbaum.[262]

Mechanical Properties of Alloys

The mechanical properties of the platinum-group metal alloys have not been studied to a great extent, although a great deal of attention has been focused on alloying to increase the strength and hardness of platinum and palladium for use in jewelry and electrical applications.

Platinum and palladium are most commonly alloyed with other members of the platinum-group metals, although there are several other metals which impart greater

solid-solution strengthening. A summary of the effect of various alloying elements on the hardness of platinum and palladium is presented in Table 15. This table was constructed by plotting the hardness data of several investigators against alloy content and then picking the hardness values from the curves. This enables an approximation of the hardness at several alloy contents although data for only a single alloy may be given. The data are presumably for the alloy in its softest condition so that in interpreting the solid-solution hardening of the various alloying elements, the variables of rate of work hardening and heat-treatment response are eliminated.

Of the alloying elements presented, chromium, nickel, and ruthenium appear to be the most effective hardeners (in platinum). Silicon also is an extremely effective hardener. The four elements, arsenic, boron, silicon, and phosphorus, in addition to imparting high hardness, form low-melting eutectics with platinum, and, in the case of the latter three, with palladium and all of the other platinum-group metals.

Jedele[263] reports that small additions, on the order of impurity levels, of phosphorus and sulfur to platinum and palladium result in a significant increase in strength and reduction in ductility both at room temperature and 850 C.

Voronow[264] also reported that the addition of 0.1 per cent silicon to platinum increased the hardness from 25.2 to 132 Bhn.

Information on the effect of alloying elements in what would be considered "impurity levels" on the mechanical properties of the platinum metals is rather scarce. Some insight into the effect of impurities on mechanical properties can be gained by examining the tensile data for the various commercial grades of platinum and palladium. Platinum is produced in four grades, Grade 1 containing 99.99 per cent platinum and the other grades containing increasing amounts of the other platinum metals; namely, rhodium and iridium. Grade 4 platinum contains at least 1 per cent of other platinum-group metals plus nickel, calcium, and silicon. Compared with an annealed tensile strength of 18,000 psi for Grade 1 platinum, tensile strengths of about 20,000-22,000 and 30,000 psi have been recorded for Grades 2 and 4 platinum, respectively.[7] The tensile strength of pure palladium is about 27,000[7] psi as compared with 28,000[7] to 30,000[45] psi for commercial palladium. These data, unfortunately, give no indication of the effect of dissolved interstitials, oxygen and hydrogen, on the properties of these metals.

The effect of systematic additions of other platinum-group metals to platinum has been studied by several investigators. Table 16 is a summary of their data. The variations in properties are most likely due to differences in the purity of starting materials, heat-treatment condition, and fabrication history.

In addition to the data in Table 16, data are also available on the properties of commercial alloys. These are far too voluminous and specialized to be mentioned here. The Platinum Metals and Their Alloys[7] contains tensile and hardness data for numerous alloys of commercial interest. In addition, company data sheets describing dental, jewelry, and electrical alloys are excellent sources for property data.

Although there are no property data available for alloys of the refractory platinum-group metals, it should not be assumed that there are no alloys of these metals available. In many cases, iridium and ruthenium alloys are used in applications requiring extremely high hardness, such as pen nibs; information from the patent literature on these alloys does not disclose what is considered significant property data.

TABLE 15. EFFECT OF ALLOY ADDITIONS ON THE HARDNESS OF ANNEALED
PLATINUM AND PALLADIUM

Alloy Addition	Hardness of Platinum, VHN, After Indicated Addition, weight per cent			References	Hardness of Palladium, VHN, After Indicated Addition, weight per cent			References
	1.0	5.0	10.0		1.0	5.0	10.0	
Silver	48	80	160	(266)	46	63	77	(7)
Gold	50-55	100	142	(267)	46	50	56	(7)
Copper	50-55	90	130	(11), (268), (269)	50-52	72	90	(7)
Chromium	50-55	125	212	(270)	50-52	70	102	(275)
Cobalt	50-55	92	135	(271), (272)	--	--	--	--
Iron	45	65	90	(273)	49	62	80	(276)
Manganese	--	--	--	--	53	85	79	(277)
Nickel	50-55	105	185	(7)	50-52	80	130	(7)
Iridium	50-55	99	139	(274)	50-52	68	85	(274)
Palladium	45	62	77	(274)	--	--	--	--
Rhodium	48	70	92	(274)	48	57	68	(278)
Ruthenium	60	130	190	(274)	52	90	169	(274)
Osmium	60	120	175	(274)	49	62	80	(274)
Antimony	--	--	--	--	50-52	73	102	(7)
Silicon	70	225	--	(264)	--	--	--	--

TABLE 16. EFFECT OF ADDITIONS OF PLATINUM-GROUP METALS ON THE TENSILE STRENGTH OF ANNEALED PLATINUM

Alloy Composition (Balance Platinum), weight per cent	Ultimate Tensile Strength, 1000 psi	References
Platinum	18	(274)
5 iridium	40	(274)
10 iridium	55	(274)
10 iridium	77	(279)
15 iridium	75	(274)
20 iridium	100	(274)
20 iridium	99	(279)
25 iridium	125	(274)
30 iridium	160	(274)
5 palladium	34	(7)
10 palladium	45	(7)
15 palladium	49	(7)
20 palladium	52	(7)
25 palladium	53	(7)
30 palladium	54	(7)
35 palladium	54	(7)
40 palladium	53	(7)
3.5 rhodium	25	(274)
5 rhodium	30	(274)
5 rhodium	35.2	(6)
10 rhodium	45	(274)
10 rhodium	46.2	(6)
10 rhodium	66	(279)
13 rhodium	50.6	(6)
20 rhodium	70	(274)
20 rhodium	59.4	(6)
30 rhodium	66.0	(6)
3 ruthenium	42	(274)
5 ruthenium	60	(274)
10 ruthenium	85	(274)
10 ruthenium	110	(279)

Some elevated-temperature mechanical properties of platinum and palladium alloys have been determined.

Reinacher[55] determined the 20-hour rupture stress of three platinum alloys, platinum-5 iridium, platinum-4 palladium, platinum-5 rhodium, at temperatures up to 1250 C. All three alloys showed an improvement in 20-hour rupture stress over pure platinum, the iridium alloy being superior up to 500 C and the rhodium alloy being slightly superior at higher temperatures.

Bennett[6] has studied the short-time creep behavior at 1400 C of platinum and platinum-rhodium alloys containing up to 40 per cent rhodium. The addition of rhodium markedly increased the 1- and 10-hour rupture stress over that of pure platinum. The difference between the 10-hour rupture stress for 20 and 40 per cent rhodium alloys, however, was only 50 psi, indicating that the proportionately greater improvement in creep strength occurs with the addition of only a few per cent rhodium; further additions contribute relatively little to the creep behavior. Bennett also observed that the addition of rhodium reduced the grain growth under stress, thus reducing the grain-boundary sliding which leads to brittle fracture. However, the addition of 5 per cent rhodium did result in intercrystalline cracking. The report did not mention whether such cracking persisted in the higher rhodium alloys.

Although no extensive grain growth and grain-boundary sliding were observed by Bennett in the platinum-rhodium alloys, it should be pointed out that examination of failed platinum-rhodium thermocouple wires has revealed grain growth resulting in grains as large as the wire diameter and attendant grain-boundary sliding.

Other investigations of the creep properties of platinum-platinum-group metal alloys have been made by Albert and Sadowski[3] and Stauss[58]. Albert and Sadowski investigated the stress-rupture properties of platinum-10 ruthenium, platinum-10 iridium, and platinum 10, -20, and -40 rhodium alloys at 927 C.

This study revealed that the platinum-10 ruthenium alloy is far superior to platinum and the other alloys on the basis of rupture life at a given stress level. The addition of 10 per cent iridium resulted in somewhat better properties than did the addition of 10 per cent rhodium. The addition of 20 and 40 per cent rhodium increased the rupture life considerably, when compared with the platinum-10 rhodium alloy, with an attendant loss in ductility. This is not entirely in agreement with Bennett's data, which show only a very slight improvement in creep properties with rhodium additions above 10 per cent.

Stauss[58], in a study of platinum-10 rhodium and platinum-10 iridium alloys at 1100 C, showed that the iridium alloy has slightly better creep properties than the rhodium alloy except at very low stress levels, where both alloys have approximately equivalent rupture levels. Both of the alloys have considerably better creep properties than pure platinum. Stauss observed that both the platinum-10 iridium and platinum-10 rhodium alloys showed a change in slope in the log stress versus log/rupture time curve at a rupture time of about 10 minutes. He observed that this break corresponded to the change from transgranular to intergranular fracture, and attributed this to a propensity to oxidation of the alloy. Another break, resulting in a decreasing slope, is observed at a rupture life of about 10,000 minutes. This increase in rupture strength presumably is due to strengthening by oxidation.

Child[57] has studied the effect of additions of gold and gold plus 0.5 per cent
rhodium on the creep characteristics of platinum at 900 C. The addition of 0.5 per cent
rhodium increased the 100-hour rupture stress by a factor of about 1.5, or increased
the rupture life at a given stress level by about 4 or 5 times, without affecting ductility.
The addition of gold also improved the creep properties of platinum; an addition of
5.0 per cent gold increasing the 100-hour rupture stress by greater than a factor of 3.
The addition of gold also resulted in intercrystalline cracking. An addition of 0.5 per
cent rhodium to the platinum-gold alloys did not appreciably alter the creep character-
istics or the tendency toward intercrystalline cracking.

An interesting development in improving the creep characteristics of platinum
wires has been reported recently. Middleton, Pfeil, and Rhodes[8] have reported that
sintered platinum has properties superior to those of platinum prepared by conventional
techniques.

Creep-rupture tests of cold-drawn wires showed that the rupture life of conven-
tionally prepared platinum was 120 hours at 1400 psi, whereas the sintered platinum
had a rupture life of 670 hours at 5000 psi. More important, the elongation during
testing was approximately 10 per cent in 20 centimeters for conventionally prepared
platinum at 1400 psi, while the sintered platinum had less than 1.0 per cent elongation
at 5000 psi. The sintered platinum had a fine fibrous structure after testing compared
with the large-grained structure usually observed in conventional platinum.

More recent developments along these lines have been made by fabricating sin-
tered platinum-10 rhodium and platinum-10 rhodium-0.025 oxide alloys that appear to
have especially good creep resistance. Commercial-sintered, dispersion-hardened,
platinum alloys with increased creep properties and excellent thermoelectric proper-
ties are now available for thermocouples. The increased strength at temperature re-
duces the number of failures due to insufficient strength in the platinum leg of
thermocouples.

Belyaev[265] also has reported greatly increased strength with no reduction in
ductility in sintered platinum wire hardened by dispersions of Al_2O_3, BeO, BaO, and
ZrO_2 in concentrations up to 0.5 per cent.

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